THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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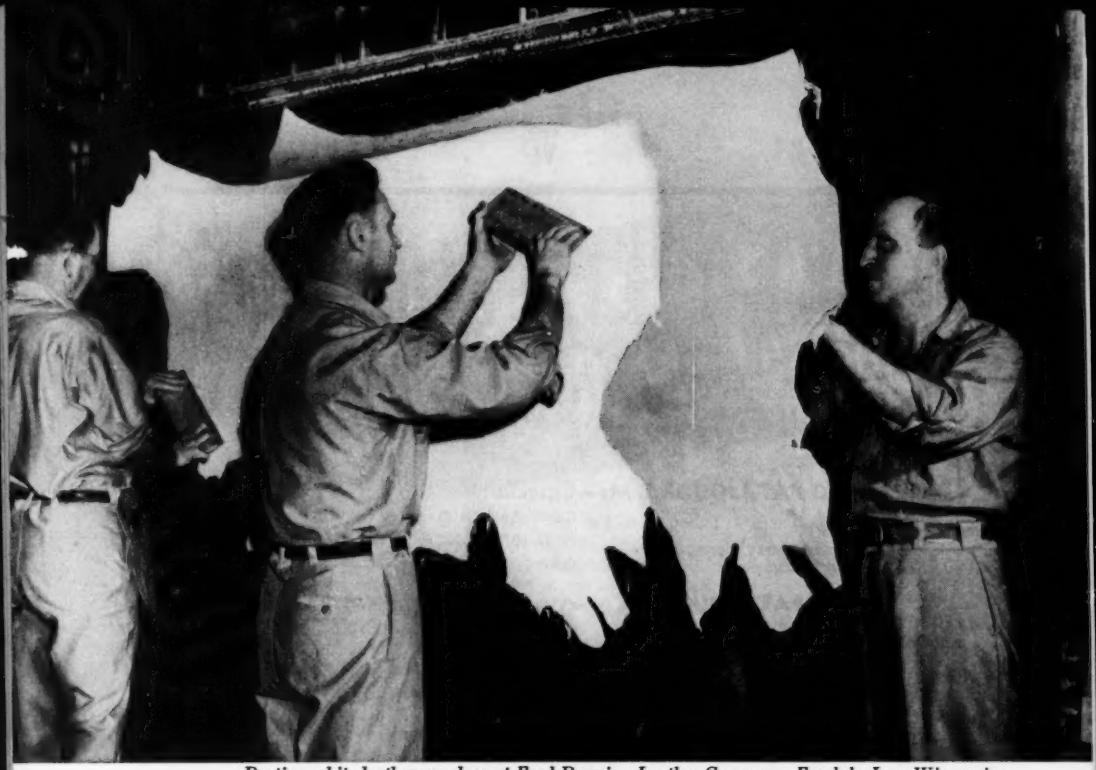

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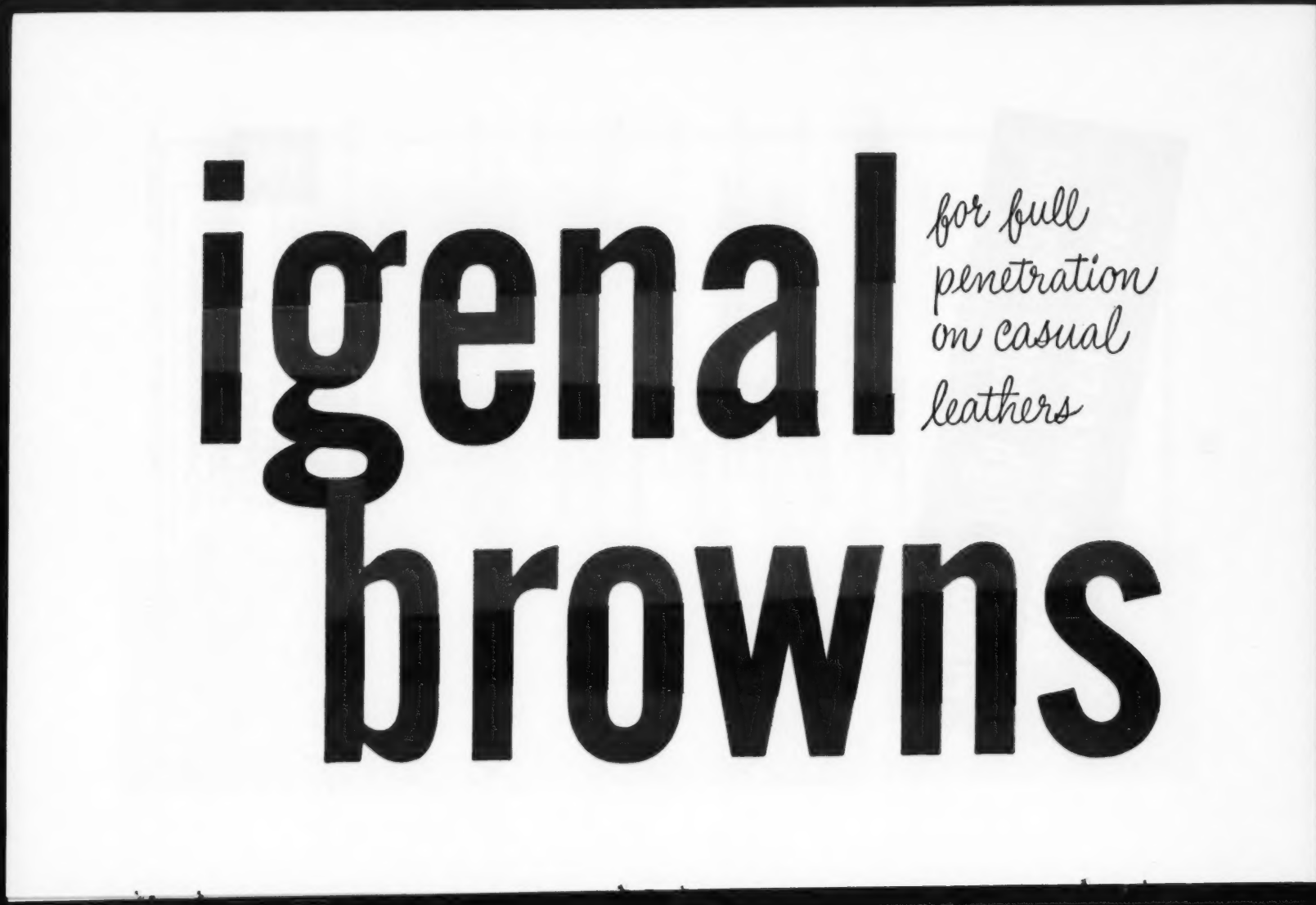
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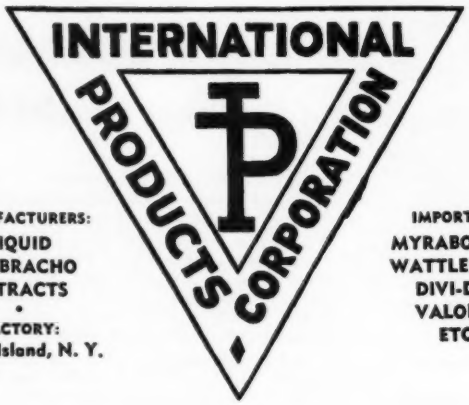

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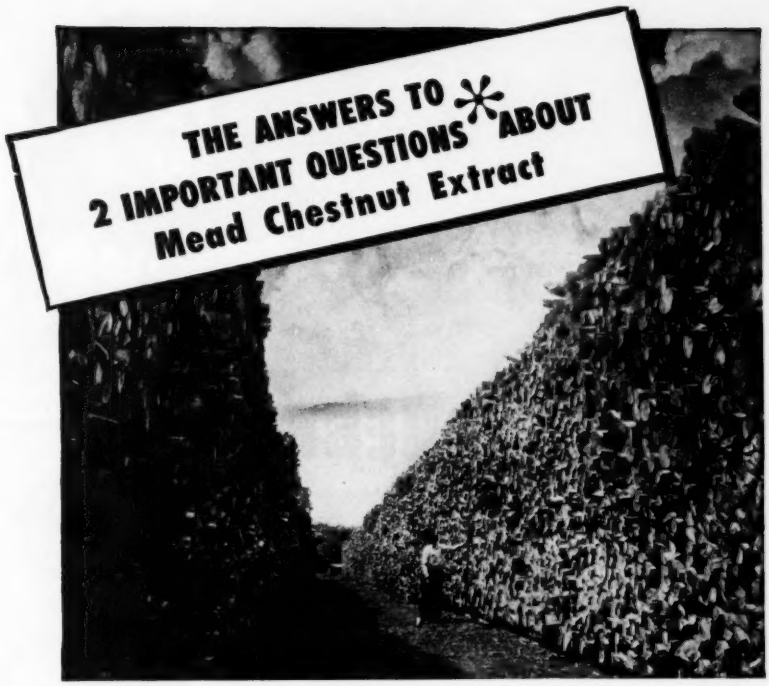

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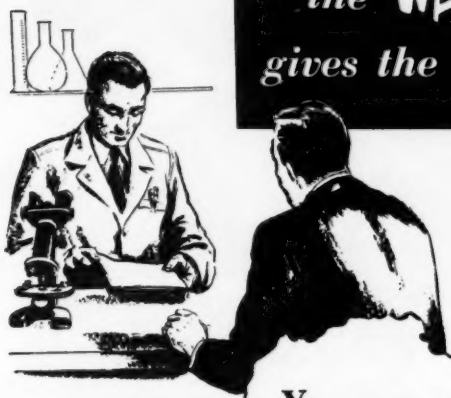

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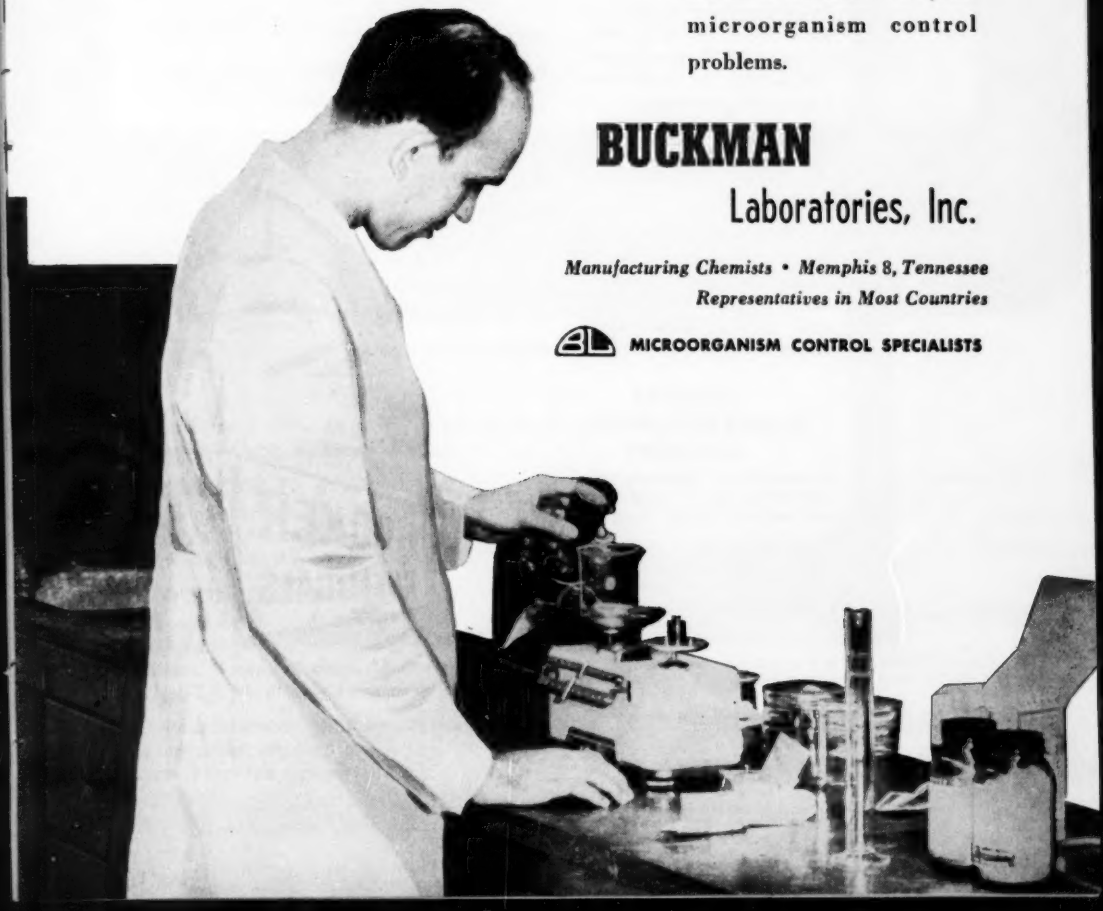

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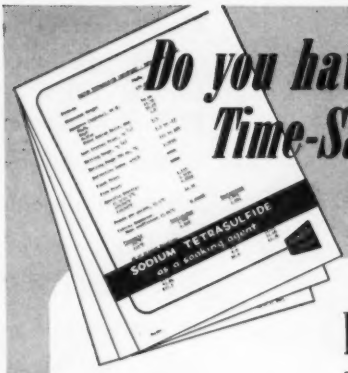

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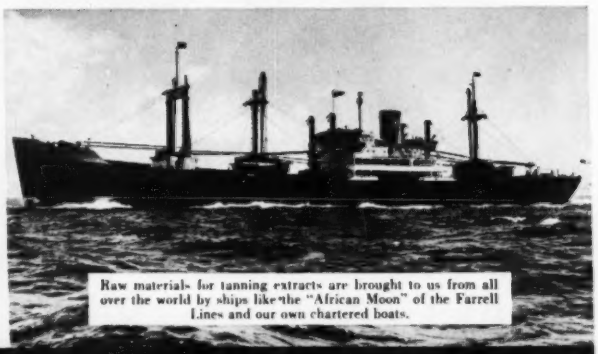

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VOL. XLIX AUGUST 1954 No. 8

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Council

R. G. Henrich, Surpass Leather Company, 9th and Westmoreland Streets, Philadelphia 40, Pennsylvania.

H. R. Wilson, B. D. Eisendrath, Memorial Laboratory, 702 Racine Street, Racine, Wisconsin.

J. R. Kanagy, 9922 Sutherland Road, Silver Spring 5, Maryland.

Mieth Maeser, United Shoe Machinery Corporation, Research Division, Balch Street, Beverly, Massachusetts.

Dominic Meo, Jr., Salem Oil and Grease Company, Salem, Massachusetts.

BUREAU OF EMPLOYMENT

Old established Eastern manufacturer is interested in securing the services of residents of the middle west, also of Canada, familiar with pigment and other specialties for the tanner's use. Write in detail concerning age, marital status, experience and compensation desired. All replies will be held in strict confidence. Address Box DA122, c/o Secretary, American Leacher Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

VIENNA CONGRESS

The Vienna Congress for Tanning Chemistry and Technology will meet in the Palais Auersperg, Vienna, September 5th to 12th, 1954. 59 cont ibutors have already indicated their intention of participating in the program, which will extensively cover Tanning Chemistry and the Manufacture of Leather.

COUNCIL MEETING MINUTES

JUNE 6, 1954

BEDFORD SPRINGS HOTEL
BEDFORD, PENNSYLVANIA

The meeting was called to order by President Turley at 11:00 P. M. Present were Messrs. Turley, Flinn, Meo, Collins, Wilson, Kanagy, Henrich, and O'Flaherty. Mr. Ross was absent.

The minutes of the meeting held on February 11, 1954, were given final approval.

Dr. Flinn reported on the progress of the technical committees.

Council discussed the position of the A.L.C.A. in participating in the Commonwealth Joint Services Committee for the establishment of common methods; it was decided to wait until such time as the matter again might become active and then request that the A.L.C.A. be given representation on the committee.

Dr. Flinn suggested that invididuals or committees should not act for the Association but should act through Council. The matter was referred to the meeting of the new Council.

Dr. Turley advised of a letter from Dr. Harvey suggesting a committee be appointed to handle problems arising in between the International Union of Leather Chemists Societies Meetings. It was decided that these problems

should be sent to the office of the Secretary and he in turn will refer them to the Chairman of the Co-ordinating Committee.

The meeting was adjourned at 11:30 P. M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary.*

COUNCIL MEETING MINUTES

JUNE 9, 1954

BEDFORD SPRINGS HOTEL
BEDFORD, PENNSYLVANIA

The meeting was called to order by President Flinn at 2:15 P. M. Present were Messrs. Flinn, Turley, Wederbrand, Thorstensen, Kanagy, Wilson, Meo, Henrich, and O'Flaherty.

Dr. O'Flaherty gave a resume of the meeting held on Sunday, June 6. Council agreed that when the chairmen of the different committees are requested to give a statement on policy for the Association, his reply should first be presented to Council through the Secretary.

Dr. O'Flaherty's resignation as Secretary was accepted. He was then re-appointed as Secretary for another term through June, 1956.

The Board of Tellers, Messrs. Downing, Maloney, and Stahnke, counted the ballots and advised Council that the following members were elected:

President-Elect—E. B. THORSTENSEN

Council—M. MAESER
DOMINIC MEO

The retiring Councilors are Messrs F. Leslie Collins and Chester Ross.

Mr. Meo reported on the Annual Meeting and advised Council that the actual expenses are within the budget. A slight increase in revenue is expected.

It is believed that a large number attended the meeting without registering. The matter was referred back to the Convention Chairman for his recommendations to be given at the next Council Meeting.

Mr. Meo requested Mr. Nelson to write each exhibitor and obtain his opinion about the exhibit. Dr. O'Flaherty reported that most of the exhibitors agreed that they obtained full value of the exhibit and would be interested in repeating it again.

The arrangement of the program for next year was discussed. It was felt that it would be necessary to:

1. either cut the number of technical papers
2. have concurrent meetings
3. to abide strictly to the time limit allotted each paper.

Council agreed that it would be better to eliminate a few papers and to abide to the time limits than to run concurrent meetings. Dr. O'Flaherty passed on a suggestion he received that the number of papers be limited from each place. The matter is to be considered at the next Council Meeting.

The question of whether papers for presentation at the Annual Meeting that are submitted to the Committee after the date line should be rejected was discussed and referred back to the Committee.

The next Annual Meeting will be held at the New Ocean House, Swampscott, Massachusetts on May 22 through 25.

Suggestions for 1956 Annual Meeting place were made. Council agreed that the meeting could be held in late June in 1956.

Mr. John Teas resigned as Ways and Means Chairman. Mr. Oscar Wederbrand was appointed by Dr. Flinn to be the new chairman.

Mr. Williams reported he had 14 papers (approximately 5 Journals) on hand plus the papers of the Convention.

The National Bureau of Standards has requested that the slides presented with their paper be re-produced in color in the Journal. Mr. Williams will obtain an estimate on the cost from Mr. Brassington. The matter will be considered when more information is obtained and presented at the next Council Meeting.

Dr. Flinn reported that he is re-writing the J15 Method and it will be a provisional method. It will be published in the July issue.

The revised edition of the Physical Testing Methods will be printed and sent to members.

Mr. Thorstensen suggested that the Association obtain a public address system to be used at the Annual Meetings. Dr. O'Flaherty will obtain estimates on the cost and report at the next Council Meeting.

The following candidates were accepted to Active status:

David M. Balfour	Joseph R. Milano
William Fiedler, Jr.	Lucien Sellet
George B. Hinson	Frank F. Stamberg
Sam R. Hoover	Abraham Turow
G. H. W. Humphreys	Jack Zeitlin

Mr. Thorstensen was appointed to review the roster of Associate members and advise as to those that he thinks are eligible for Active membership.

Council wishes to thank Dr. Turley for his work and time he has given while President. They also extend their appreciation to Mrs. Henrich and her committee for such a well planned program for the ladies.

The next Council Meeting will be held in late October or early November. A definite date will be set by a mail vote.

The meeting was adjourned at 3:15 P. M. Repsectfully submitted,

Fred O'Flaherty, *Secretary*.

MINUTES OF MEETING OF SUPERVISORY COMMITTEE ON TANNIN ANALYSIS

A meeting of the Supervisory Committee on Tannin Analysis was held at the Beford Springs Hotel June 6, 1954. The meeting was called to order at 11:15 A. M. by the Chairman, A. N. Kay. The following members and guests were present: *Members*, R. E. Barnwell, T. C. Blair, G. V. Downing, J. M. Hinkle, A. N. Kay, K. H. Knight, F. F. Marshall, L. Rayfield, J. S. Rogers, G. W. Stanbery, D. Williams, and J. F. Wagoner. *Guests*, C. W. Beebe, I. D. Clarke, R. E. Merritt, E. M. Nilachione, H. A. Nordstrom, G. L. Somer, C. G. Telander, H. G. Turley, and J. M. Zito.

Mr. Kay reported on the status of the revised methods. These appeared in the March and April issues of the Journal. To date two minor changes have been suggested. Mr. Williams stated that any further changes would have to be made at once in order that the publication of the Methods Booklet can proceed on schedule. Therefore Mr. Kay set the deadline at June 30, 1954 for any further corrections from the members.

The report of the Sub-Committee on Lignosulfonates was the next consideration. In the absence of Co-chairmen Jány and Wolfe, Mr. L. Rayfield gave a brief summary of a report which had been drawn up by Mr. Jány. Inasmuch as this report had not been considered or approved by the whole Sub-Committee Mr. Kay suggested that a meeting of the Sub-Committee be held and the report carefully considered. The report should then be submitted to the Committee by mail for comment. Mr. Rayfield also advised that Messrs. Jány and Wolfe did not wish to continue as Co-Chairmen of the Sub-Committee. Mr. Kay then appointed Mr. Rayfield Temporary Chairman with instructions for the Sub-Committee to select their own permanent chairman.

The only new business up for consideration was the matter of further study on the method for the determination of copper. Several indicated dissatisfaction with the present Xanthate method, but after a brief discussion the matter was tabled for the present.

There being no further business the meeting adjourned at 11:45 A. M.

J. F. WAGONER, *Acting Secretary.*

REPORT OF THE PHYSICAL TESTING COMMITTEE

BEDFORD SPRINGS, PENNSYLVANIA

JUNE 6, 1954

The following members were present:

F. L. COLLINS, *International Shoe Comanpy*

C. W. Beebe, *Eastern Research Laboratory*
W. T. Roddy, *Tanners' Council Laboratory*
R. M. Lollar, *Tanners' Council Laboratory*
G. V. Downing, *Leas & McVitty*
S. S. Kremen

Guests:

E. M. Filachione
J. M. Zito, *U. S. Testing Company*
K. H. Knight, *Graton & Knight*

Changes in Methods

Since the revision of the Physical Testing Methods was completed and published in the Journal of April, 1953, the committee has done very little active work.

As the methods are being used changes are being suggested. Some of the suggestions which have been made and the action taken by the committee follows:

Water Penetration, Dynamic P. 31

It has been suggested that the speed of this machine should be increased to 200 rpm instead of the present 90 rpm. Preliminary tests indicate that the increased speed has very little influence on the results, particularly when leathers with high water resistance are being tested. If the increased speed is to be used some precautions will have to be taken to prevent the water from splashing over the pan or into the specimen.

No comparative interlaboratory investigation has ever been conducted on this test. Its acceptance was based almost entirely on the single set of tests reported in the Journal, Vol. XLII, No. 8, 1947. The committee decided that it would be advisable to run comparative interlaboratory tests using the present speed of 90 rpm to determine the inherent variables in the method itself and the variations which would be found between the various laboratories. Comparative tests at 200 rpm. would be run in one or two laboratories. Dr. Lollar was asked to prepare a test program to be carried out by laboratories at the Bureau of Standards, United Shoe Machinery Corporation, Quartermaster Department, Eastern Regional Research Laboratory, and the University of Cincinnati.

Stitch Tear Strength—Double Hole

Due to the high variability of leather, it is necessary to test a large number of specimens to obtain significant results when the present method is used. A specimen with five holes instead of two has been suggested. The greater number of holes gives a more integrated value, i. e., a value less apt to be

effected by local variations, than the two hole method and fewer specimens are required.

Just before the meeting the man who suggested the use of a five hole instead of a two hole specimen reported that preliminary analysis of the data which he had from tests comparing the two methods indicated that the five hole specimen was no better than the two hole specimen, i. e., that the variability between specimens was as great when the five hole, as when the two hole, specimen was used.

Shrinkage Temperature

The method for determining the shrinkage temperature of leather was not included in the revision because it was felt that no pressure apparatus was available which would operate with water only and measure shrinkage temperatures above 100°C with the required accuracy and with the necessary safety.

Such a piece of apparatus has been developed by Dr. Kremen and is being considered by the committee.

Dr. Kremen is preparing a publication which will be submitted to the Journal in a short time. The committee decided to do no further work on the method until Dr. Kremen's results have been studied.

Flex Tension Test for Leather

It has been proposed that a method such as suggested by T. J. Carter and J. R. Kanagy in their paper "A Flex Tension Test for Leather", J.A.L.C.A., XLIX, 1, P. 23 be considered by the committee. This is a form of endurance method which measures the life of leather when it is repeatedly flexed while under tension. The Association has no endurance method and this test would fill that need.

There seemed to be very little interest on the part of other laboratories in the matter. The committee decided to take no action at the present time.

Future Work

Most of the members of the committee feel that our chief effort should be devoted to the improvement of our present methods rather than in the development of new ones. All phases of testing should be studied; including sampling, specimen cutting, the mechanics of the test, and the errors which are apparent and hidden, the variability within the method itself, and the variations between laboratories.

The whole committee will participate in this work with various members being requested to take the lead in the different aspects of the work. No definite program will be started until fall.

MIETH MAESER, *Chairman*
Physical Testing Committee

THE FIFTIETH ANNUAL MEETING

The Fiftieth Annual Meeting of our Association was held at the Bedford Springs Hotel, Bedford, Penna. from June sixth through June ninth. It was the largest annual meeting in the history of the Association, with three hundred and fifty registered members and one hundred and fifty ladies and guests attending.

The afternoon and evening of June sixth were filled with Committee meetings, broken by a reception by the officers just prior to the dinner hour. The meeting proper was opened Monday morning with an address by the President, which follows:

OPENING REMARKS BY THE PRESIDENT—Dr. H. G. Turley

The Meeting will please come to order.

Fellow Members, Guests and Visitors: We welcome you this morning to our Fiftieth Annual Meeting and hope you will enjoy the beautiful surroundings of the Pennsylvania countryside and that the weather will smile upon you. We sincerely hope that you will enjoy the program provided for you by our Convention Committee that has made some interesting new departures this year.

In giving you an accounting of the past year, I must first announce to you the loss by death of six members, namely, Paul Bernhardt, Alfons Jaeger, Herman Ritter, Alexander Saxe, Swanie Rossander, and a Mutual member, Ramon Paniker, Honorary President of the Spanish Society of Leather Chemists. I will ask you to pause for a silent moment in tribute to the memory of our former members and friends.

The Association continues to show a satisfactory state of growth. We are happy to report that since a year ago, we have gained eighty new members. This is a very satisfactory record and we must congratulate all members for bringing in new faces and personalities to add vigor to our Association. Keep up the good work.

While thinking of our new members, we are not unmindful of the debt we owe, as an Association, to the unfailing service of our old members, and your Council recently unanimously agreed to grant Life Memberships to eight of our members who, by continuous membership, have supported the Association for forty years. These members are: James Connelly, Guy Creese, Otto Haas, Jerome Lang, Frank Marshall, Ralph Porter, Harry Smith and Joseph Stodola. We shall present them with Life Membership Certificates at the banquet tomorrow.

Our finances for 1953-54 are in sound condition. The balance sheet will be published in the Journal for July. Our total income was $32,749. and our total expenses $27,460., leaving a balance of $5,288. of income over expenditure. This situation reflects great credit on the Chairman of the Ways and Means Committee, Mr. John Teas, and our Secretary, Dr. Fred O'Flaherty. It also attests to the sound policy laid down by my predecessor, Dr. R. Koppen-

hoefer. A part of our satisfactory accounting is due to our adverstisers, and we publicly thank them for their support. Have you observed what a great change in the advertising quality and style has taken place in our Journal compared with a few years back? It means something today to reach at least nine hundred members and many times that number by association. Our Journal is in good condition, and elsewhere it has been stated to be the outstanding leather chemists' journal of the world, and I believe that its high eminence has been reached because of the impeccable character of our editors, and we owe a lot to them. Our continued thanks are due to Mr. Dean Williams for so unselfishly giving of himself and his time to uphold the standards of our Journal during the past seventeen years.

In 1947 we decided to join the International Union of Leather Chemists Societies and play our part in fostering good will among the leather chemists of the world, and to deliberate with them on attaining universal methods for the analysis and recognition of the tanning materials of the world. We are entitled, on account of the size of our membership, to send seven delegates to the International meetings which are held biannually. At the first two post-war meetings, we were represented by two delegates but, infortunately, at the meeting last year in Barcelona, we had no representation. To correct this condition, Council voted to send one official delegate to the meeting at Stockholm in 1955 and to supply the funds—$1,000.—to underwrite the expenses of the delegate's trip. Our financial condition permits us to do this, and I am sure this action will be with the approval of the membership. We have the honor to represent the International Union of Leather Chemists Societies on your behalf, as President-Elect.

When the Leather Industries of America was organized, our Association set up a committee of experts in many fields—scientific, business, economics, advertising—to be of help to this publicity organ of the Tanners' Council. Due to lack of activity this committee was discharged, but I feel I can say for the members that we are always ready to do what we can as individuals or as an association to be of help to the L.I.A.

The technical committees have been very active this year, not so much on chemical problems but on drawing up methods for publication. Our early Presidents stressed greatly the need and value of committee work and indeed it was the spendid work of the committees which, in the early days, established our methods for the analysis of tans, on a sound basis. However, today—as in the past—much work seems to fall on the shoulders of the older, experienced members, and I will repeat the plea expressed by several of the early Presidents of asking new members, especially the younger members, to come forward and volunteer to work on our committees. You will find the experience rewarding and valuable, and your sense of belonging to the Association will be increased by the giving and taking necessary when working on a committee. As I just

mentioned, the techincal committees have been active in writing up new methods. This has taken about two years and has been a real task. So much of this burden falls on the President-Elect, in his capacity of Coordinator of Technical Committees, that the Association is greatly indebted to Dr. E. S. Flinn who has organized the writing and editing of the methods. These new methods started to appear in the Journal for April 1953, are continuing, and should be complete in July, covering over two hundred pages and one hundred and forty-two methods. Many committees and their chairmen have worked hard in trying to provide the Association with the finest methods available for the examination of everything connected or concerned with the making, examination, and testing of leather. We would mention to you the work of Mr. M. Maeser on the Physical Testing Methods, Mr. Arthur Kay on the Analysis of Tanning Materials, Dr. H. B. Merrill on Tannery Chemicals, Mr. Robert Adams and Dr. L. Seligsberger on Mineral Leathers, Mr. Jerome Rogers on Vegetable Leather Analyses and Mr. Paul McKee on Leather Finishes. Also, the Association must acknowledge the help given the committee chairmen by the individual members of the committees. To them we say, "Thank You."

As to the adoption of these methods, there have been some changes in all the methods, therefore, Council decided to publish them on a "Provisional" basis, and they remain on this basis for a year in conformity with the By-Laws. Will not the members study these methods during the coming year and forward any criticisms to the Technical Coordinator so that there will be a general agreement by the Association of the correctness of the methods before they become Official?

As to our program this year, we have made some departures which should be of interest to you. We have one day, i. e., today, devoted to the reading and discussion of the thirteen scientific papers offered. The range of subjects covered is wide and should interest all of you. Then, tomorrow morning we have a session of a half-day given over to a panel of authorities to describe and discuss research. Now the question of research for the leather industry has been a constant theme in our Association. Many of my predecessors have expressed themselves in their annual addresses on the need for research. My immediate predecessor, Dr. R. Koppenhoefer, stated in bold terms the need for research, and contrasted the state of affairs in leather versus the petroleum industry, pointing out that in the latter case a definitely higher percentage of technical people were employed. He also criticized the fact that much research applied to leather was done by suppliers and not by the industry. While some of the chemical supply houses have done excellent research in certain aspects of leather, they have naturally neglected other areas of considerable importance to the industry. In other words, perhaps the internal research of the industry by the industry has been neglected in the past. As long ago as 1915, L. Levi expressed the need for research. In 1923

C. Smoot expressed the pleasure of our Association on the decision of the Tanners' Council to establish a research laboratory, and in this year, a research laboratory was established at Cincinnati. For an industry of the size of the leather industry, this research laboratory was but a modest beginning. Since that time, there has been no unusual increase in the research effort, and the leather industry has not kept pace with other industries. Already in 1934, i. e., after eleven years of research by the Laboratory, G. McLaughlin drew attention to the fact that the application of science in the leather industry had not kept pace with the known scientific principles. In 1946 our Mr. Dean Williams pointed out the need for more research to meet the challenge of the new industrial changes. Finally, in 1948 T. Oberlander posed before the Association the question of organizing research on an adequate scale for the industry, and called attention to the confusion existing between basic and process research, and suggested in a broad way the need for a considerable expansion of research in the leather industry.

Today the question of research is receiving more attention from the industry on account of the realization of the competition from substitute materials which have emanated from research frequently done by industries that devote a larger portion of their income to research. As the retiring President, it seemed to me that it is thoroughly appropriate to bring the question of research before you and, I hope, the management of the leather industry. We, therefore, organized in this program a panel dealing with research by successful research exponents, and tomorrow morning will be given over to this symposium. Dr. Fogler of Arthur D. Little will talk on the organization and management of research; then will follow Prof. Dewitt Dearborn of the Carnegie Insitute of Technology on expenditures for research; after, Dr. Wakelin, Director of Research of the Textile Research Institute of Princeton, will tell us of some of their work in fiber technology for the cotton and wool trades; finally, Mr. Irving Glass of Tanners' Council will conclude the meeting with a talk on current ideas of the management of the leather industry for expanding and widening out the scope of the research program.

Leaving the topic of research, we come to the every-day problems of the leather making industry. This is what is usually called the "practical" side of leather making. In the past there was much good-natured criticism of the chemist by the practical tanner in that the former did not talk the every-day language of the tanner. This was put briefly by F. H. Small in 1921 when he stated, "The chemist has surrounded himself with an atmosphere of mystery which has tended to create misunderstanding and, frequently, complete misapprehension of the functions and extraordinary value of the chemist."

To remedy this stituation a start was made in 1952 at our meeting at Swampscott. A half-day program was undertaken by the New England Tanners' Club. This was quite successful and we were approached by a number of members and workers of the leather industry to repeat the performance.

Encouraged by this volume of interest, we are devoting, on this occasion, one full day's session to be taken over by the practical groups of the industry. Consequently, this conference on leather making is being organized on a national basis by the three industry clubs, namely, The Delaware Valley Tanners' Club, The New England Tanners' Club and The Tanners' Production Club of Wisconsin, under the chairmanship of Mr. W. Morris. The chief groups of leather manufacturing have formed their committees and will participate on a group basis. We hope all of you will take part because we invite free discussion from the floor, and we would like to see managers, superintendents, chemists and foremen all discussing leather making in a free spirit of give and take.

A word as to our social arrangements. The reception held on Sunday evening last year was a great success and so many members wished for this to be continued. The Convention Committee came up with the idea of inviting the suppliers of materials, apparatus and services to exhibit their goods in a dignified way for a small fee. This income will be given to the Convention Committee in payment for the reception. We acknowledge the participation of the following firms in the exhibition: American Cyanamid Company, Battelle Memorial Institute, Diamond Alkali Company, Dow-Corning Corporation, Engineering Specialties, Leather Industries of America, Murmac Manufacturing Company, Rohm & Haas Company, Salem Oil & Grease Company, U. S. Testing Company.

Now I must close this account of the Association, but I do want to be serious and say to you that in looking over the situation in the leather industry today, I find that in this phase of competition from artificial and substitute materials heavily supported by research, the successful tanner is the one making the finest leather; in fact, leather of such quality that is extremely hard to imitate with synthetic materials. The play or, perhaps, the drama of national and world markets goes on before your eyes all the time and if I may parody a phrase, I would say, "The product's the thing."

The program was somewhat different from those of previous meetings inasmuch as it was divided into three phases of Association activity. Two aspects, technology and research, were appropriately represented by eighteen papers. The third phase, namely the practical side, consisted of an open discussion of practical problems of tanning and leather manufacture.

The technical papers presented were:

HISTOLOGICAL STUDY OF THE HOG SKIN DEHAIRING PROCESS

By H. Wang, Nehema Maynard, and F. L. DeBeukelaer.
American Meat Institute Foundation

PORES IN LEATHER

By Robert R. Stromberg and Max Swerdlow
National Bureau of Standards

DETERMINATION OF AMIDE NITROGEN IN COLLAGEN AND OTHER PROTEINS

By Edward F. Mellon, Samuel J. Viola, and Sam R. Hoover
United States Department of Agriculture

A PILOT-PLANT STUDY OF THE PROCESS FOR TREATING HEAVY LEATHER WITH POLYISOBUTYLENE AND OTHER POLYMERS

By Rene Oehler, John H. Davis, and Raymond A. Kinmonth
National Bureau of Standards

THE PREPARATION AND TANNING PROPERTIES OF PHENOLIC DERIVATIVES OF LIGNINSULPHONIC ACID.

By H. Borden Marshall, Mary Krizsan, W. A. Kenzie, and Alison M. Wilson

THE PREPARATION AND TANNING PROPERTIES OF PHENOLIC DERIVATIES OF LIGNINSULPHONIC ACID (Continued)

Application of the Cresol Derivative to the Retanning of Chrome Leather.

By W. R. Kenzie and Alison M. Wilson

ALUM RETANNAGE OF VEGETABLE-TANNED INSOLES IMPROVES THEIR SERVICEABILITY

By C. W. Beebe, W. F. Happich, W. S. Kip, and J. S. Rogers
United States Department of Agriculture

THE RELATIVE STABILITY OF DIFFERENT TYPES OF SOLE LEATHER TANNAGES UNDER HUMID STORAGE CONDITIONS

By Seymour S. Kremen, R. Lee Southwood, and Blaine L. Lucas, Jr.
University of Cincinnati

RESISTANCE OF WHITE UPPER LEATHER TO BREAKDOWN BY PERSPIRATION

By WILLIAM T. RODDY and ROBERT M. LOLLAR
University of Cincinnati

HYDROLYTIC DETERIORATION OF SIDE UPPER LEATHER

By WILLIAM T. RODDY and JEROME JANSING
University of Cincinati

THE CHROME TANNING MECHANISM

By ROBERT STUBBINGS
Lehigh University

THE DYEING OF CHROME TANNED LEATHER IN TERMS OF THE SURFACE COLOR PRODUCED

By GEORGE STRAUSS and ROBERT STUBBINGS
Lehigh University

THE EVALUATION OF TANNERY WASTES

By MARK M. LUCKENS

The Tuesday morning session was devoted to research. Four speakers discussed research, each from a different angle, and their presentations constituted a well rounded viewpoint of this subject. The speakers were:

I. R. GLASS, *Executive Vice-President*
Tanners' Council of America

BENJAMIN FOGLER, *Associate*
Arthur D. Little, Inc.

J. H. WAKELIN, *Director of Research*
Textile Research Institute
Princeton University

DEWITT DEARBORN, *Professor, Graduate School*
Industrial Administration
Carnegie Institute of Technology

Wednesday was given over to the discussion of the practical problem of tanning and leather manufacture under the auspices of the Delaware Tanners, the Wisconsin Tanners and the New England Tanners Production Clubs

with Wendell Morris as chairman and C. David Wilson as moderator. Members of the panel were; Charles A. Martin, representing the Calfskin Division, W. R. Lotz, representing Side Leather, James K. Koeniger, representing Upholstering Leather, Reuben C. Heurich, Goat and Kid Division, Charles T. Cares, Sheepskin Leather, and Arthur N. Kay, representing Sole Leather.

Two years ago a similar symposium was held under the auspices of the New England Tanners Production Club, and at that time soaking of hides and skins occupied the entire period. This year the panel devoted most of the discussion to liming. In all probability this portion of the program will appear as a supplement to the Journal.

In the way of entertainment the square dance, held at the barn Monday evening, was such a success that the barn floor should have been at least twice its size for comfortable dancing.

Tuesday afternoon the annual golf tournament, this year conducted by Harold Y. Miller and Robert Weldon, was participated in by approximately one hundred members and guests. All were enthusiastic about the course, speaking of it as one of the finest on which the tournament has ever been played. The winners and prizes were as follows: J. S. Morrison, Medalist-Leather Jacket, H. R. Miller, Jr., Low Gross Open-Teas Memorial Cup and Leather Jacket. C. M. Morrison, Low Gross Active-Senior Cup and Leather Jacket. L. E. Monnier, Low Net Active—L. A. Cuthbert Memorial Cup and Patent Handbag. H. D. Sentkowski, Low Net Open—Reilly-Whiteman-Walton Memorial Cup and Calf Handbag. In addition to the above, minor prizes were won by: H. R. Miller, James Byron, Frank Chadwick, M. Lindsay, Guy Mitchell, M. A. Buckley, S. C. Walker, R. Adams, I. C. Sommerville, W. Cashman, E. F. Gross, W. Petersen, Robert Welch, E. S. Flinn and J. H. Wakelin.

The prizes were presented at the annual banquet Tuesday evening. Guest speakers at the banquet were stylists and designers, Mr. and Mrs. William D. Phelps, who pointed out that the material rejected because of lack of uniformity by the pragmatist is frequently just the material desired by the artist.

Life Membership awards were made to several members of over forty years standing. These awards went to James Connolly, Guy Creese, Otto Haas, Jerome Lang, Frank Marshall, Ralph Porter, Harry Smith, and Joseph Stodola. Dr. H. G. Turley, retiring President, was also awarded a life membership. The Alsop Award went to Dr. R. M. Lollar, the presentation being made by Mieth Maeser. Mr. Maeser's remarks and Dr. Lollar's acceptance speech are given below.

PRESENTATION OF THE ALSOP AWARD

Mrs. and Dr. Turley, Mrs. and Mr. Phelps, Ladies and Members of the American Leather Chemists' Association, and Guests:

Dr. Turley, earlier this year, asked me to serve on the Awards Committee; and it was a pleasure to participate in the selection of a candidate for the Alsop Award for 1954.

It is my very pleasant duty, tonight, to present the Alsop Award for the year to Dr. Robert M. Lollar.

Bob: This award is given to you by the River Plate Corporation at the suggestion of the Awards Committee and with the approval of the Council of the American Leather Chemists' Association for the many contributions which you have made to leather technology and to the leather industry.

You have made so many contributions in such a variety of ways that I will not attempt to ennumerate them at this time.

May I say simply: First, that your work as a member of the various committees of the American Leather Chemists' Association; Second, that the many papers you have published in our Journal and in the various trade magazines; Third, that your early and pioneering use of statistical methods in leather research testing and in the leather industry; Fourth, that your work at Cincinnati as a research man and a teacher of the young men in whose hands the future of the leather industry will partially fall; and, Fifth, that personal admiration in which you are held—are the things for which the Association wishes to honor you.

May I present this watch as a symbol of the professional and personal regards in which you are held by the members of this Association.

ACCEPTANCE OF THE ALSOP AWARD

By Robert M. Lollar

TANNERS' COUNCIL RESEARCH LABORATORY

University of Cincinnati
Cincinnati 23, Ohio

I accept this, the 1954 Alsop Award, with considerable personal humility for I know full well that a scientist today does not stand alone. In large measure that which you cite in your presentation is based upon the work of all of you and upon the work of leather chemists of yesterday. The unselfish contributions of W. K. Alsop, in whose honor this award is named, to the leather industry are typical of the background out of which our present work can develop.

I should also like to acknowledge my indebtedness to the many graduate students who have contributed to that which you recognize this evening. Only those who have experienced the stimulus of working with eager, inquiring students can fully appreciate what this has meant.

Highberger, Doherty, Koppenhoefer, Roddy and O'Flaherty—certainly no greater quintet of leather chemists could have been available as teachers. You recognize the results of their efforts in making this award to me.

Finally, I acknowledge my indebtedness to industry and to the culture which has made the work you have cited possible. The unique industry-University cooperation which has supported our Laboratory, the interest of the firm who makes this award possible, all these are representative of our indebtedness to our cultural heritage which acknowledges the worth of the individual. I pray to God that I may in some small measure be able to be worthy of this honor given me and contribute to the preservation of this heritage. In this spirit, Mieth, I accept this award from you, my friend, among these friends of many years.

The Ladies Committee, headed by Mrs. Reuben Henrich and ably assisted by Mrs. Harold G. Turley, Mrs. Edwin S. Flinn, Mrs. Ralph B. Eddy, Mrs. Charles Martin and Mrs. I. C. Somerville, provided a full program for the distaff side. Prizes were awarded for various contests such as bridge, canasta, putting, shuffle board and others.

The results of the election were announced as follows: President Elect, E. B. Thorstensen. Council Members, Dominic Meo and Mieth Maeser. Secretary and Treasurer, Fred O'Flaherty, was relected by Council for the ensuing year. Dr. H. G. Turley completed his term as president and is succeeded by E. S. Flinn.

The Association has seen its largest growth under President Turley and, under the chairmanship of E. J. Flinn, the Committee on Methods has completed the Revision of the Methods. These are now being published in the Journal.

Under the leadership of John J. Teas, Chairman of the Finance Committee, the Association has also shown financial growth. All in all, the two years under the Presidency of Dr. Turley show a record of accomplishment of which he and the Association may well be proud.

Swelling of Collagen and Modified Collagen*

By J. M. Cassel and E. McKenna

National Bureau of Standards

Abstract

A detailed study is presented of the swelling in aqueous media of collagen (hide powder) and of collagen modified by acetylation, deamination, esterification, and by tanning with different concentrations of syntans, and of aldehyde, vegetable, and mineral tanning agents. The tanning agents studied are formaldehyde, quinone, glyoxal, methyl glyoxal, chromium, zirconium, quebracho, chestnut, and gambier. Some theoretical aspects of the tanning action which may occur are discussed on the basis of the swelling data presented.

*Presented at the Golden Anniversary Meeting, Cincinnati, Ohio, June 7, 1953.

The swelling is measured in aqueous media in which the pH was varied from 1.8 to 12.0. The weight of the swollen materials is used as a measure of the swelling which occurred.

Formaldehyde-tanned collagen is shown to be resistant to swelling in either acidic or basic media. Other tannages may suppress swelling in acid but are not as effective as formaldehyde in basic media.

The swelling of collagen in aqueous media is shown to be temperature dependent; this dependency is most pronounced in media where the Donnan equilibria and osmotic pressure forces are operative, e. g., pH 2 and 11.5. In water, measurable protein swelling was greater at 22°C than at either 1°C or 37°C.

1. Introduction

One of the interesting properties of collagen, the protein constituent of hide and leather, is its ability to imbibe water when placed in an aqueous medium. The imbibition and resulting swelling are markedly affected by the content of the aqueous medium and external conditions so that pH, salt content, temperature, etc., all affect the amount of swelling. Inasmuch as conversion of hide into leather by tanning decreases the degree of swelling in a given medium, it would appear that detailed study of the swelling of tanned and untanned collagen in aqueous media might offer some insight into the chemical nature of the tanning process. This method of approach has received considerable attention previously by many workers [1], [2], [3] who have studied only a few of the factors affecting swelling.

In general, swelling in neutral solution may be considered to result principally from the hydration of accessible polar groups of the collagen. In acidic or basic solution, however, the primary contributor to the swelling of protein is the osmotic effect resulting from the Donnan equilibrium, which is set up as the protein surface acts as a semipermeable membrane to the diffusible ions of the solution. When the concentration of ions is greater on the protein side of the membrane, water diffuses into the protein and swelling occurs. The effect of neutral salt solutions may be to increase or decrease swelling. The influence of neutral salts is considered [4] to arise from the effect of the salts on the cohesional and adhesional forces of the water and protein. When cohesional forces between water molecules are less than adhesional forces between protein and water, swelling is increased. Some salts, i. e., $CaCl_2$, produce ions which appear to have specific effects on the protein. Such salts are not of interest here.

In this paper are presented data in the form of graphs which relate the swelling over a range of pH from 1 to 13 of the protein hide powder and of hide powders treated by deamination, by esterification, by acetylation, and by tanning reagents of the aldehyde, mineral, vegetable and syntan types. Data are also included to show the effect of temperature on the swelling of hide powder in water and in media where maximum swelling occurred at room temperature.

2. Methods of Measuring Swelling

The hide powder used in this swelling study was a commercial product (Lot No. 26). To obtain a more uniform product for the swelling measurements, it (as well as the modified hide powders) was ground in a laboratory Wiley mill to pass a 20-mesh screen. Samples were allowed to condition at a constant temperature and humidity and then were stored in tightly stoppered containers.

The protein materials with their swelling media were contained in weighed 50-ml centrifuge tubes. Eight-tenths of a gram of dry protein material was weighed on an analytical balance and transferred to the centrifuge tubes. Approximately thirty milliliters of water was blown into the tube in a small stream from a wash bottle in a manner designed to wet as much of the protein material as possible. Materials which proved difficult to wet were centrifuged a minute at 3000 rpm and the tube contents then thoroughly stirred with a glass rod. The desired amounts of 1N hydrochloric acid or sodium hydroxide were added to each tube from a microburette and an additional fifteen milliliters of water added while at the same time vigorously stirring with a glass rod. Tubes containing alkali were stoppered tightly with corks and the glass-cork joint heavily coated with paraffin to reduce carbon dioxide absorption.

The tubes were then stacked upright at 22° C for twenty-four hours an interval which was found to be sufficient for the attainment of equilibrium. The weights of the swollen materials were determined by centrifuging at a speed of 3000 rpm for five minutes, and carefully braking the centrifuge to a stop so as not to disturb the protein particles. Then, after decanting a portion of the supernatant liquid for pH determination, the remaining supernatant liquid was removed by suction. It was found that by centrifuging at this speed the supernatant liquid could be removed readily without removing significant amounts of protein. The pH determinations were made with the glass electrode buffered at pH 4.01, 7.0, and 9.18, and with the use of the special alkali electrode in the pH range above 9. The tubes were then weighed to the nearest milligram on an analytical balance and the weight of the swollen protein determined by difference. The swelling was expressed as the total weight of swollen material per gram of hide substance.

In order to follow the effect of temperature on the swelling of hide powder, it was necessary to use a different technique since the heat generated in the centrifuge was sufficient to interfere with the measurements at 1°C. For this purpose the volume rather than weight of the swollen material was determined and the centrifuge was not employed. Volumes of the swollen materials at the different temperatures were determined by reading the volume directly from the calibrated centrifuge tubes in which the hide powder and swelling media were contained.

To reduce the extent of protein solution at the higher temperature in acid and base, the hide powder for these experiments was ground to pass a 4-mm screen rather than the 20-mesh screen used in preparing the rest of the materials studied.

3. Methods of Modifying Hide Powder

Deaminization of hide powder was accomplished according to the technique of Thomas and Foster [5] as modified by Bowes and Kenton [6]. The hide powder was reacted for three days with a nitrous acid solution, a fresh nitrous acid solution being used each day. During the reaction the temperature was maintained at 20°C. Previous work [7] had shown that this treatment would reduce the lysine content of hide powder from 5.3 per cent to less than 0.9 per cent while the arginine content was virtually unaltered. The nitrogen content of the product after deamination was 17.4 per cent, representing a loss of 0.4 per cent in nitrogen presumably through amino group cleavage.

The procedure of Frankel-Conrat and Olcott [8] as modified by Gustavson [9] was followed in esterifying hide powder. Thirty grams of hide powder were reacted for one week at room temperature in three liters of methanol wichh was 0.1 normal with respect to hydrochloric acid. The esterifying mixture was transferred to a water bath (temperature 1°C) and sufficient sodium hydroxide solution was added slowly in a dropwise manner with constant stirring to neutralize the hydrochloric acid. The neutralized esterifying solution was then removed by suction and the esterified product washed with water four times for fifteen minutes. The excessive swelling of the esterified product made water removal after each washing difficult. Acetone proved much preferable to alcohol in the final dehydration prior to drying at room temperature. The nitrogen content of two batches prepared in this fashion averaged 17.6 per cent, which indicates appreciable solution of the protein did not occur during the treatment. Methoxyl determinations were made by the standard micro technique as modified by Steyermark [10].

Hide powder was acetylated by treatment with a 5-per cent solution of acetic anhydride in acetic acid for 8 hours at room temperature and by treatment with a 50-per cent solution of acetic anhydride in acetic acid for 72 hours at room temperature. The former procedure according to Green, Ang, and Lam [11] acetylates the amino groups of collagen while the latter acetylates the amino and the hydroxyl groups. The acetylated hide powders were extracted with acetone in a Soxhlet extractor for 4 days to remove reactants not held by the protein. The total acetyl contents of the acetylated hide powders were determined by refluxing the acetylated sample in sulfuric acid and then steam distilling the refluxed mixture to liberate acetic acid which was titrated with weak alkali [11].

With a few exceptions, all of the tanning procedures adopted were similar in at least two main respects. Except in a few instances, a twenty-four-hour

tanning period was adhered to, during the first and last four hours of which the solutions were thoroughly agitated. Secondly, the tanned products were washed overnight in running tap water and then a minimum of six times in separate 1-liter volumes of distilled water. Each distilled water washing lasted one hour during which time the mixture was agitated. The wash water was removed by suction. It was felt that this procedure would remove at least the majority of uncombined tannins.

Formaldehyde tanning was accomplished at pH 8 (phosphate buffer) except in those instances when it was desired to study the effect of tanning at different pH's. The esterified hide powder was exposed to the formaldehyde tanning solution for four hours in contrast to the twenty-four-hour period allotted the other formaldehyde tannages. The formaldehyde contents of formaldehyde-tanned hide powders were determined by the method of Highberger and Retzsch [12].

The pH during tannage with glyoxal and methyl glyoxal (pyruvic aldehyde) in aqueous media was maintained near 7 by a 0.1 N acetate buffer. Methyl glyoxal tannages were of nine days duration. When tanning in acetone and dioxane, uncombined tannin was washed free with acetone followed by ethyl ether.

Para-benzoquinone was used as the quinone tanning reagent and during tanning the pH was maintained near 6.5 by addition of small amounts of alkali.

A basic chromium sulfate one-bath procedure was followed in tanning with chromium. The equilibrium pH of all chrome tanning solutions was between 4 and 4.7.

A zirconyl sulfate tanning agent* was used to tan with zirconium. The equilibrium tanning pH was 1.8–2.0.

Vegetable-tanned hide powders were obtained by tanning with gambier, chestnut, and sulfited quebracho extracts. The equilibrium tanning pH in each instance was between 4.4 and 4.7.

The three types of syntan extracts used were an acidic naphthalene type (Syntan A), a sulfonated phenol-formaldehyde type (Syntan B), and a lignosulfonic acid type (Syntan C). Tannage with the acidic naphthalene type was carried out in the pH range 3 to 3.5 while equilibrium with the latter two syntans was between 4 and 4.8.

4. Results and Discussion

4.1 *Swelling of Hide Powder*

In figure 1 are shown the data obtained by the centrifuge method relating the swelling of hide powder to the pH of the aqueous medium. Minimum swelling occurs in the vicinity of pH 4.5 to 5, the isoelectric range of the protein [2], while maximum swelling occurs in acid at pH 2 and in base at approxi-

*Rohm and Haas Zircotan N.

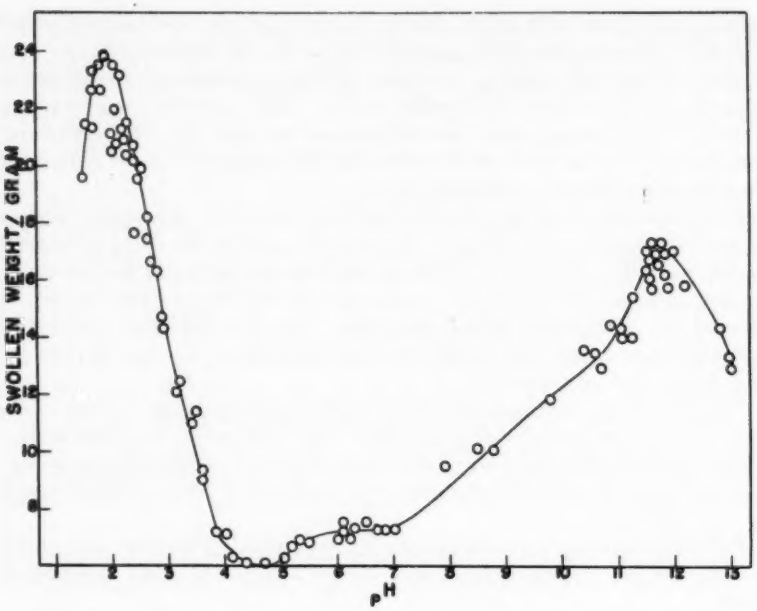

FIGURE 1. Effect of pH on the weight increase of hide powder in unbuffered solutions.

mately pH 11.7. The maximum swelling in acid is greater than in base, a result in agreement with previous work [13] in which hide powder was used. The swelling in the isoelectric range is considered a swelling of imbibition where hydration of particular groups occurs and the great increase in water take-up in the acidic and basic ranges is attributed almost entirely to the Donnan effect [14]. The hide powder surface acts as a semipermeable membrane permitting diffusion of hydrogen and chloride ions. As the ionized carboxyl group accepts hydrogen ions in the acidic titration of the protein, chloride ions are simultaneously drawn across the membrane to maintain electrical neutrality; a similar explanation satisfies for the swelling which occurs in base where the formation of sodium proteinate occurs. In either acid or base as long as the total concentration of ions is greater on the protein side, water continues to diffuse into the protein and swelling occurs. In addition to the Donnan explanation for points of maximum swelling, the factor of protein solution which reduces the measured swelling, becomes more important in the extreme acidic and basic ranges.

The precision of the determinations ranged from a standard deviation of 0.2 gram/gram of hide substance on an individual measurement in the region of minimum swelling to that of 0.6 gram in the region of maximum swelling.

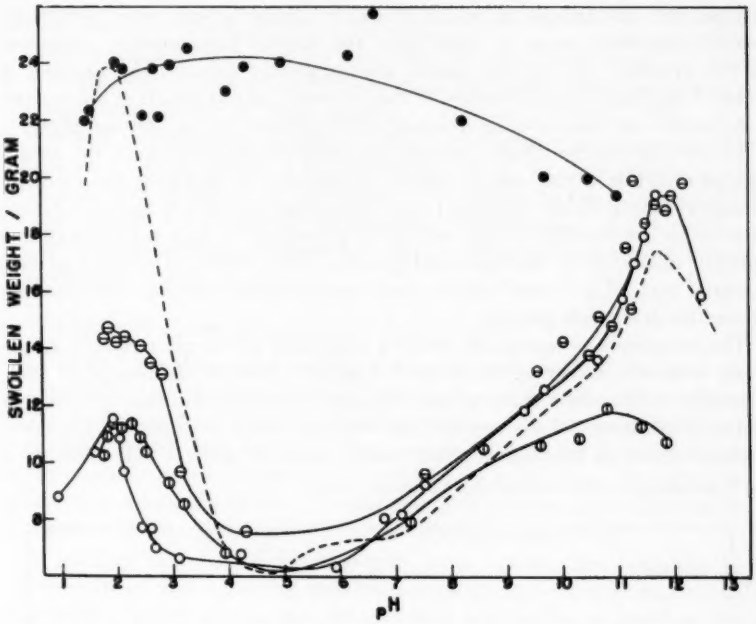

FIGURE 2. Effect of deaminization, acetylation, and esterification on the swelling of hide powder.
○ deaminized, ⊖ acetylated (0.47 millimole acetyl per gram hide substance), ⓘ acetylated (1.60 millimole acetyl per gram hide substance), ● esterified, – – – control hide powder.

4.2 *Effect of Deaminization, Acetylation, and Esterification on Swelling of Hide Powder*

In figure 2 the swelling characteristics of deaminated, acetylated, and esterified hide powders are compared with the untreated material. The considerably diminished swelling capacity of the deaminated and acetylated samples at corresponding acidic pH's correlates with the removal of the amino group by the nitrous acid treatment or its blocking by the acetylation procedure. The flow of water into these samples, which is due to the Donnan effect, is lessened since the positively charged amino group has been replaced in one instance (deaminization) by the hydroxyl group and in the other instance (acetylation) by a modified peptide type group. The swelling capacity of the sample in which acetylation was restricted mainly to amino groups (0.47 millimole acetyl per gram hide substance) is somewhat greater in acid than that of the sample in which both amino and hydroxyl groups were acetylated (1.62 millimole acetyl per gram hide substance). The deaminated

sample and the sample in which primarily amino groups were acetylated swelled somewhat more in alkali than the control hide powder. Blocking of the hydroxyl groups with acetyl groups greatly reduced the swelling in base. This is due to inactivation of the hydroxyl groups which in the control hide powder are free to ionize in alkali and contribute to the Donnan effect.

In contrast to the effect obtained by removal or blocking of the amino groups of lysine is the rather drastic consequence of blocking the carboxyl groups as shown by the swelling curve of esterified protein in figure 2. Esterification by the Frankel-Conrat and Olcott procedure [5] is believed to be almost entirely restricted to the carboxyl groups. The methoxyl content of this material was 2.7 per cent* which would mean almost complete esterification of the free acidic side groups.

The occurrence of maximum swelling over most of the pH range, in agreement with the results of Bowes and Kenton [6], may be attributed at least partially to the elimination of salt linkages occurring between amino and carboxyl groupings of the protein, the effect of which is to permit the polypeptide chains to be pushed apart readily even at neutral pH, allowing a

*After making a correction for the methionine S-CH_3 content.

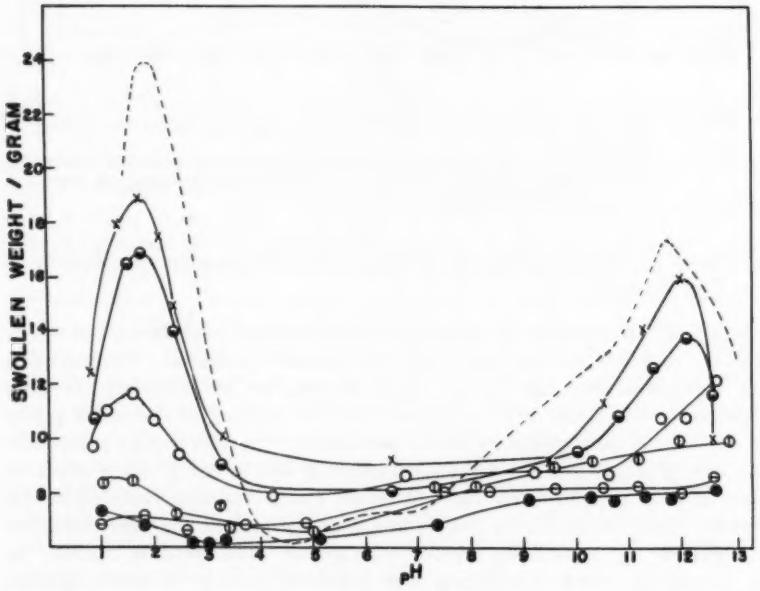

FIGURE 3. Swelling of formaldehyde-tanned hide powders.
×, 0.1 per cent CH_2O; ◒, 0.2 per cent CH_2O; ○, 0.6 per cent CH_2O; ⓘ 0.8 per cent CH_2O; ⊖, 1.2 per cent CH_2O; ● 1.9 per cent CH_2O; – – – control hide powder.

greatly increased take-up of water molecules.

The increased swelling by the esterified product is attributed by Bowes and Kenton [6] to a Donnan equilibrium effect due to electrovalent association of anions with the protein basic groups.

A certain additional contribution to the increased swelling by the esterified sample may be the result of some degradation of the hide powder toward gelatin by the esterification treatment. While the nitrogen determination on the treated and untreated samples gave no indication of a degradation, the physical appearance of the treated sample indicated that some conversion may have occurred.

4.3 *Swelling of Formaldehyde-tanned Hide Powders*

In figure 3 are shown the swelling curves for hide powders tanned at pH 8 to contain various concentrations of formaldehyde. The results are expressed as the swollen weight per gram of hide substance. As the formaldehyde content of the tanned hide powder is increased to 1.2 per cent a steady decrease in the tendency to swell is observed both in acid and in base. If, as has been mentioned earlier, one of the principal effects of tanning is to reduce swelling in aqueous media, formaldehyde seems to qualify adequately.

A primary reaction of formaldehyde with protein has generally been assumed to be that occurring with the amino groups of the protein [2]. Such combination could account for the complete suppression of swelling in the acid region. Calculation of the 1.2 per cent formaldehyde on a molar basis gives 0.4 millimole of formaldehyde per gram of hide powder or per 0.36 millimole of amino group (approximately a 1:1 ratio).

However, by comparing the data of figures 2 and 3 it may be observed that the maximum swelling in acid is approximately the same for deaminated hide powder as for hide powder containing 0.6 per cent formaldehyde. The ratio of formaldehyde combined to the amino groups of the protein is approximately 1:2 (0.2 millimole for formaldehyde per 0.36 millimole amino groups). The deaminization procedure has been shown [7] to remove almost 90 per cent of the amino groups. The similarity of the degree to which deamination and formaldehyde combination to the extent of 0.6 per cent formaldehyde reduce the maximum acid swelling of hide powder may be explained by postulating that each mole of formaldehyde condenses with two amino groups to split out water and form a methylene bridge.

In a recent paper [15] Green has postulated that only half the amino groups of collagen are reactive to formaldehyde and, further, that those reactive formed methylene bridges with primary amide groups of the protein. This theory would not seem to explain the similarity in the acid swelling of the deaminized and the 0.6 per cent formaldehyde sample referred to earlier since those amino groups not combined with formaldehyde would be free to ionize and lead to increased water absorption.

The fact that a further decrease in acid swelling is observed on increasing the combined formaldehyde from 0.6 to 1.2 per cent indicates that the additional formaldehyde bound is being held by active ionizable groups such as guanidino and amide groups.

The ability of the formaldehyde if present at least to the extent of 1.2 per cent (0.4 millimole/gram of hide powder) to completely suppress the swelling in both acid and alkaline regions would seem to be attributable to a tying together of the peptide chains, preventing their separation and hence the entry of water between them. Formation of methylene bridges involving amino and amino groups, amino and imino (peptide) groups, and amino and amide (glutamine and asparagine) groups has often been postulated[2, 16]. Bear[17] has shown that a formalin fixed rattail tendon carried through a shrinking and spontaneous lenthening cycle in warm water still retains its small angle diffraction pattern while without formaldehyde stabilization the tendon loses all discrete small angle diffraction. Bear attributes this to the ability of formaldehyde to link the protofibrils of each fibril so they do not become hopelessly disarranged during the shortening process.

The bridging concept would seem to be favored by the results obtained on tanning an esterified sample with formaldehyde. These data are shown in

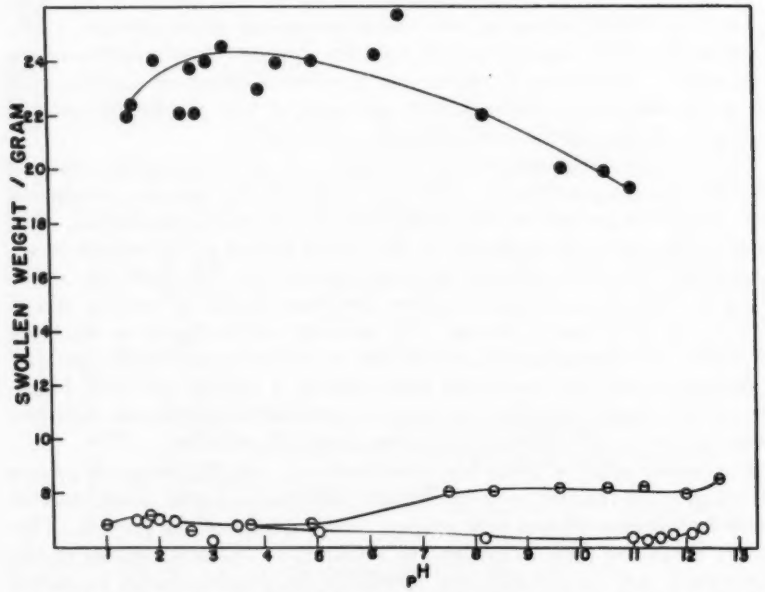

FIGURE 4. Comparison of the swelling of formaldehyde-tanned hide powder with hide powder esterified and then formaldehyde-tanned.
● esterified; ⊖ CH_2O tanned; ○ esterified - CH_2O tanned.

figure 4. With 1.4 per cent formaldehyde or 0.46 millimole per gram of sample the tremendous tendency of the esterified product to swell has been completly inhibited. If bridging does occur during tanning it must be postulated that the peptide chains of the esterified material are sufficiently in close proximity to permit cross linking. Since the dry esterified hide powder was placed directly into the formaldehyde tanning solution, it is possible tanning occurred before any appreciable swelling and hence separation of chains took place.

Because the methoxyl content of the tanned esterified product was still relatively high (2.2 per cent) an alternative explanation of these results may be taken. If the amino groups are combined with the formaldehyde and the carboxyl groups esterified, then the major polar groupings of the protein have been blocked and little tendency to take up water would be expected.

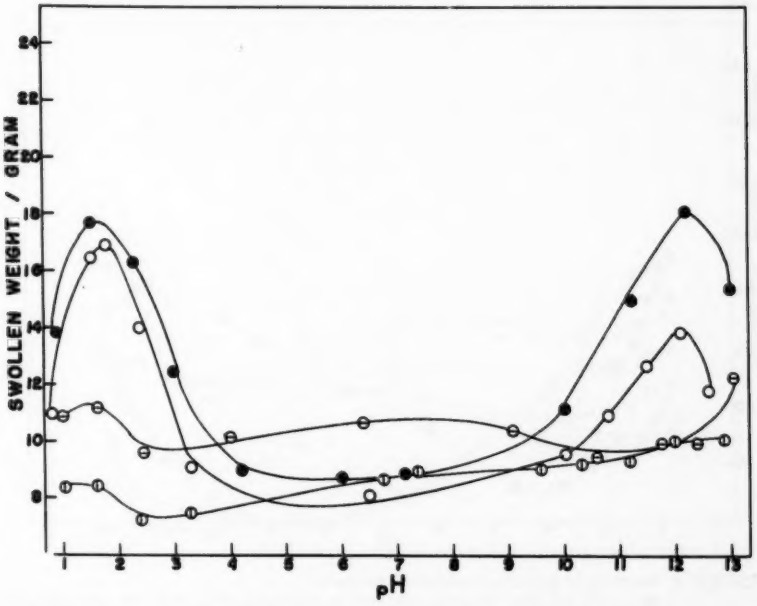

FIGURE 5. Effect of pH of formaldehyde tannage on swelling of formaldehyde-tanned hide powders.
○ , 0.2 per cent CH_2O (pH 8); ● , 0.25 per cent CH_2O (pH 2); ⓘ , 0.8 per cent CH_2O (pH 8); ⊖ , 0.9 per cent CH_2O (pH 10.5).

In figure 5 a comparison is made of the swelling of hide powders tanned at different pH's to contain approximately the same content of formaldehyde. Tannage accomplished at pH 8 seems to be more effective in suppressing swelling than that at either pH 2 or 10.5.

Tannage at pH 2 with formaldehyde is particularly ineffective in the suppression of basic swelling. Tannage at pH 10.5 while effective in the basic region is not quite as effective in the acid region as that accomplished at pH 8. It may be that some polymerization of the formaldehyde molecules occurs in this region of alkalinity rendering the per mole usefulness of the molecule less.

The apparent small increased swelling in the neutral region of some of the formaldehyde-tanned powders over that of untreated hide powder may be attributed to the lyotropic effects of some buffer salts not sufficiently washed from the samples.

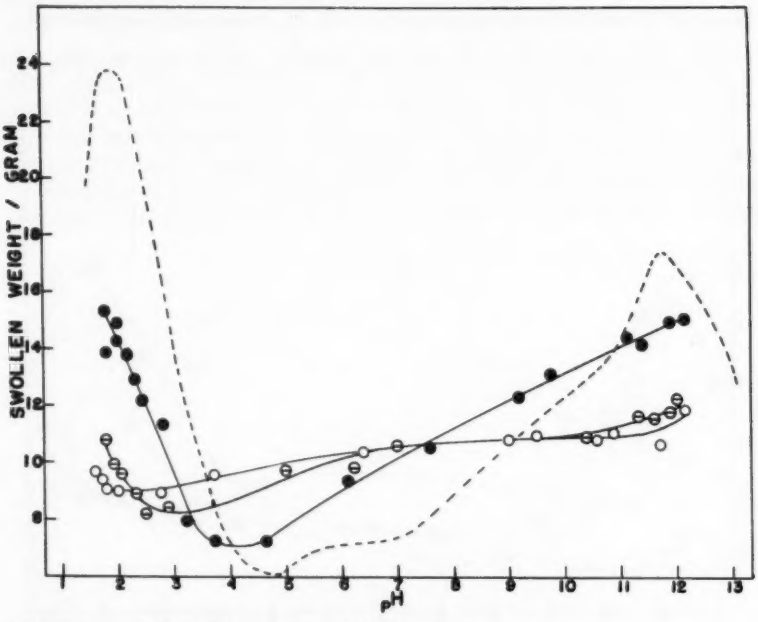

FIGURE 6. Swelling of glyoxal-tanned hide powders.
● , 2.0 per cent glyoxal (tanned in acetone); ⊖ , 3.0 per cent glyoxal tanned in aqueous media); ○ , 5.0 per cent glyoxal (tanned in aqueous media); – – – control hide powder.

4.4 *Swelling of Glyoxal and Methyl Glyoxal-tanned Hide Powders*

In figure 6 are shown the swelling curves of hide powders tanned to contain three concentrations of glyoxal. The 2-per cent glyoxal sample was tanned in an acetone medium while the remaining glyoxal samples were tanned in aqueous medium.

Since swelling in acid has been inhibited by this reagent, some combinations with the amino groups seems likely to have occurred. Suppression of swelling in the acid region is not as complete as is observed in hide powder samples which bound an equimolar amount of formaldehyde. This would be in agreement with the results of Gustavson who found glyoxal to be much less effective than formaldehyde in increasing the shrinkage temperature of raw pelt [18]. The glyoxal sample tanned from acetone had very little effect on the maximum swelling in alkali and in fact the sample swelled a little more than did untreated hide powder in the range of pH 4 to 11. While some salt formation may have occurred in this range during the swelling measurement leading to lyotropic swelling it seems more probable that attachment of a glyoxal unit permits one end of the molecule to remain free as an aldehydic group which would tend to attract water.

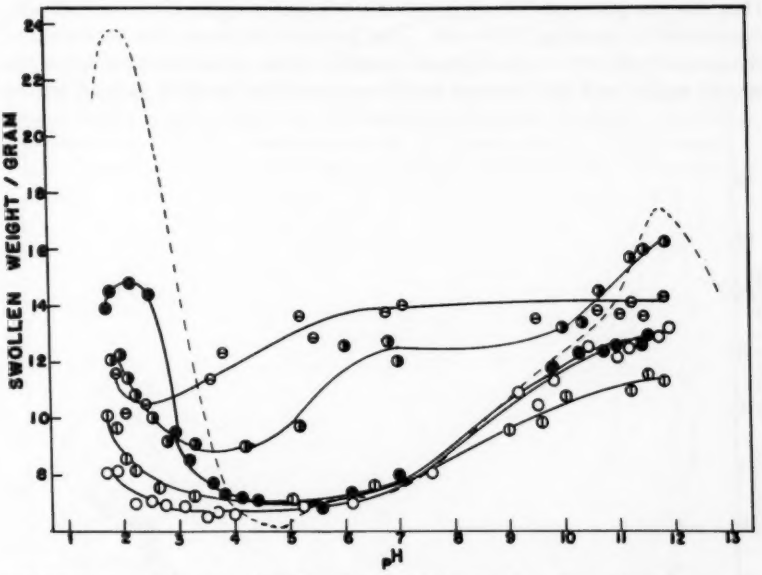

FIGURE 7. Swelling of methyl glyoxal-tanned hide powders. Tanned in dioxane: ●, 2.4 per cent; ⓘ, 9.0 per cent methyl glyoxal. Tanned in acetone: ○, 9.6 per cent methyl glyoxal. Tanned in aqueous media: ◑, 6.0 per cent; ⊖, 11.7 per cent methyl glyoxal. – – – control hide powder.

In figure 7 are shown the results of tannage with methyl glyoxal (pyruvic aldehyde) from organic and inorganic media. Tanning from either organic or inorganic media produced a material which swelled considerably less in the acid region than untreated hide powder, the tanning from organic medium being apparently more effective by this criterion. The same is true of the

basic region. On a molar basis the tannage with methyl glyoxal is not as effective as formaldehyde in suppressing acid swelling and not nearly so effective in the suppression of alkaline swelling.

Gustavson [19] has pointed out that tannage with methyl glyoxal in acetone and dioxane imparts to hide powder practically complete resistance to the proteolytic action of trypsin, whereas hide powder tanned in aqueous solutions is markedly attacked.

The marked increase in swelling in the neutral range of the products tanned from aqueous medium over that of the untreated hide powder may be due to several factors. The ash value of the dried product was higher than desirable. The product was washed by agitating it with fresh portions of distilled water which were removed by applying suction. Due to the presence of a buffer, a fairly high salt concentration was present in the tanning medium. That the inorganic ions were firmly attached was evidenced by the difficulty experienced in washing them out. The presence of these salts (acetate and phosphate buffers were used) would result in some increased swelling in the neutral region and also in some small suppression of swelling in acid region.

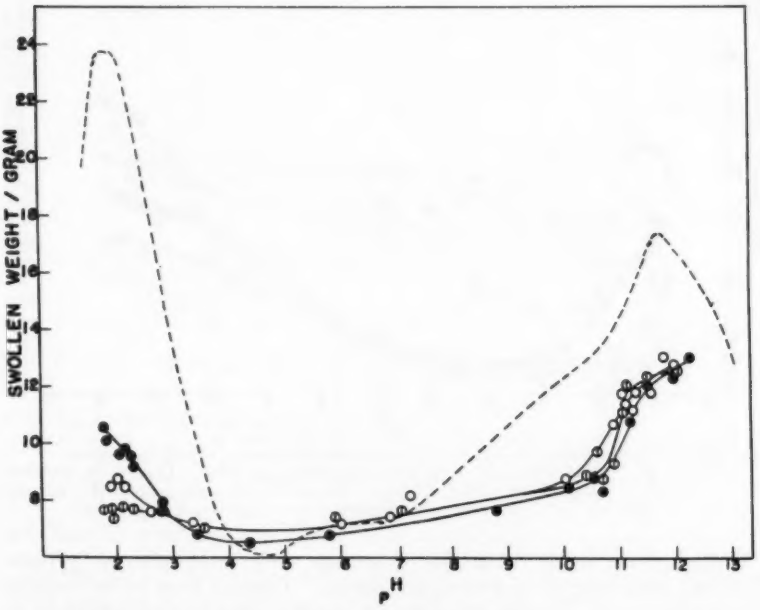

FIGURE 8. Swelling of quinone-tanned hide powders.
● . 2.5 per cent quinone; ○ , 6.0 per cent quinone; ⓘ , 9.5 per cent quinone; – – – control hide powder.

It is of interest to note that hide powder exposed to the salt buffer solutions in the absence of methyl glyoxal could readily be freed of its salt content.

The presence of the tanning molecule itself in the hide powder could lead to some increase in water take-up in the neutral range. This would indicate however that the tanning molecule remains in the hide powder after aqueous tannage in a different form than after organic tannage since swelling was not observed in the neutral range in products tanned in an organic medium.

4.5 *Swelling of Quinone-tanned Hide Powders*

In figure 8 the swelling data are plotted for hide powder tanned to contain different concentrations of quinone (parabenzoquinone). The results indicate that quinone very effectively suppresses the swelling of hide powder in acid and even though a leaching out of the quinone is obvious at pH's greater than 9 the swelling in this range is reduced to a fair extent. Expressing the quinone content on a molar basis, this tanning agent is as effective as formaldehyde in suppressing acid swelling but is nowhere near as effective in the suppression of swelling in base. It is generally assumed that the side chain amino groups of collagen play a major role in the mechanism of quinone tanning[2]. Inactiva-

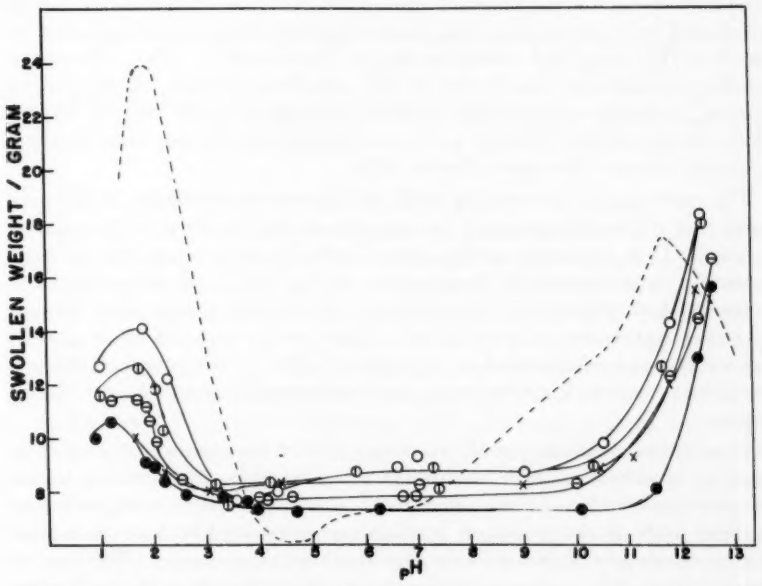

FIGURE 9. Swelling of chrome-tanned hide powders.
○ . 0.6 per cent Cr_2O_3; ⓘ , 1.2 per cent Cr_2O_3; ⊖ , 2.0 per cent Cr_2O_3;
● , 2.9 per cent Cr_2O_3; × , 4.5 per cent Cr_2O_3; – – – control hide powder.

tion of the basic groups by combination with the tanning molecule would reduce the swelling of the tanned product in an acid medium. However, Green[15] has shown that a large amount of quinone is bound independently of the amino and hydroxyl groups. Green postulates this latter tannin combination involves the peptide groups of the protein. It has also been postulated that this tanning agent cross links the polymer[20, 21] but if such is the case this cross link would seem to be broken at pH's more basic than 10.

4.6 *Swelling of Chrome-tanned Hide Powders*

In figure 9 swelling data of hide powders tanned to contain different concentrations of chromium are compared. With increasing amounts of chromium (expressed as chromic oxide) up to 2.9 per cent the effect is to steadily decrease the extent of maximum swelling in acid. In alkali obvious strong leaching of the chromium from the hide powder occurred at the more basic pH's but swelling was reduced to a considerable extent up to pH 11.7 by the presence of 2.9 per cent chromic oxide. The general effect of chrome tanning was to make more alkaline the pH of maximum swelling in base. Since it is generally believed that chromium tanning results in cross linkages which involve at least the carboxyl groups of the protein[22], the decreased swelling tendency in base of the chromed hide powders up to a pH near 11 can be attributed to inactivation of the carboxyl group which is normally free to ionize in this range and contribute to the Donnan effect. The reduction of swelling in base may also be due to the cross linking ability of the chrome tanning molecule which would restrict separation of the peptide chains. Both freeing of the carboxyl group and destruction of the cross linkages probably occurs at the more alkaline pH's.

The restriction of the swelling of the chrome-tanned materials in acid indicates that the amino groups of the protein are also involved in the tanning process. That the amino groups play a role in chrome tanning has been shown by measurements of chrome taken up by acetylated, deaminated and untreated hide powders[23]. The chrome take-up was considerably reduced by either acetylation or deamination. Combination with the amino groups has sometimes been assumed as a secondary effect of the action of chrome, the primary or initial process being combination with the side chain carboxyl groups.

Plant[24] has assumed that the minimum size of the complex which can be fixed by coordination with a carboxyl group contains 2 chromium atoms. On this basis he has calculated that 2.6 per cent chromium expressed as chromic oxide is the minimum fixation necessary to give a cross linkage of the peptide chains and a rise in the shrinkage temperature. The data of figure 9 show that a maximum suppression of swelling in acid was accomplished with 2.9 per cent chrome expressed as chromic oxide (or 1.1 milliequivalents chrome per gram of hide substance).

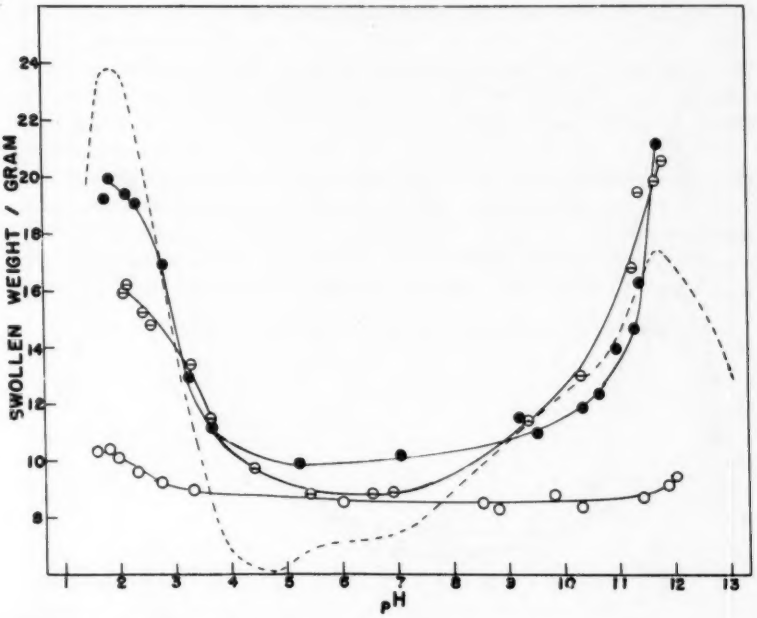

FIGURE 10. Swelling of zirconium-tanned hide powders.
●, 8.2 per cent ZrO_2; ⊖, 11.7 per cent ZrO_2; ○, 18.6 per cent ZrO_2; – – – control hide powder.

4.7 *Swelling of Zirconium-tanned Hide Powders*

The swelling of hide powders with different zirconium contents is given in figure 10. It is apparent that as the zirconium concentration is increased the suppression of swelling in the acid region is improved. The zirconium tannin content was determined by ashing the samples at 600°C for 24 hours. While the ash is almost entirely zirconium oxide, it is known that on ashing at this temperature very small residual amounts of sulfate remain[25]. Assuming the ash to be mainly ZrO_2, then an ash value of 18.6 per cent is equivalent to 1.3 millimoles zirconium oxide per gram of hide substance. In figure 9 it can be noted that almost a similar suppression of swelling was obtained in a sample containing the equivalent of 0.2 millimole of chromic oxide per gram of hide substance. Not until considerable (18.6 per cent) zirconium was held by the hide powder was any suppression of the swelling in base noted. Suppression of swelling in the basic region seems to require either blocking of the carboxyl groups or a strong cross linking which is not effected in alkaline pH. Since tanning was done at pH 1.8 and it has been observed that the zirconium tanning agent is mainly cationic[26], it is doubtful

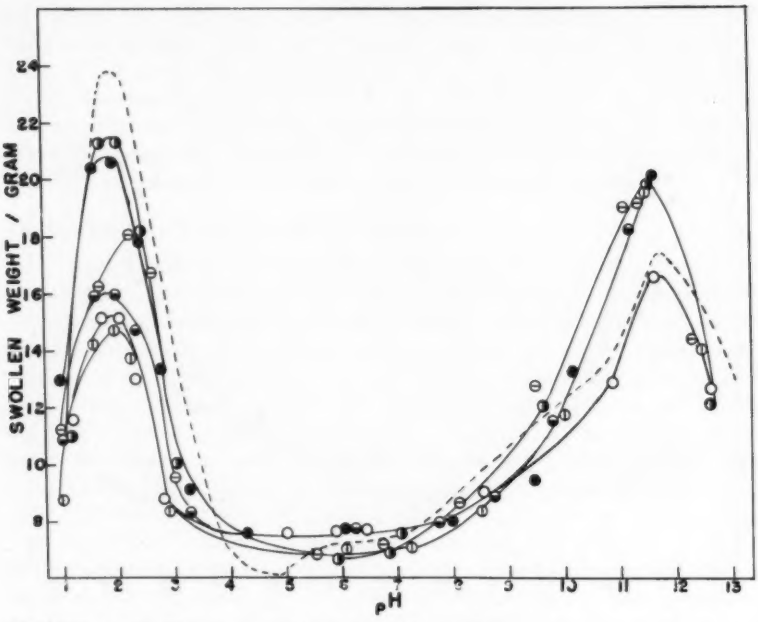

FIGURE 11. Swelling of vegetable-tanned hide powders.
● , 7.0 per cent gambier; ◒ , 16.0 per cent gambier; ⊖ , 14.0 per cent quebracho; ⓘ , 23.0 per cent quebracho; ◑ , 12.7 per cent chestnut; ○ , 28.0 per cent chestnut; – – – control hide powder.

that combination with carboxyl groups occurred because to a great extent at this pH the carboxyl groups are associated. An explanation for some of the suppression of swelling in both acid and base may be due simply to the large salt effect caused by the high zirconium concentration in the hide powders.

4.8 *Effect of Vegetable Tanning on Swelling of Hide Powders*

In figure 11 the swelling curves are compared of hide powder tanned with gambier, sulfited quebracho and chestnut. If present in sufficient concentration each of these tannin extracts showed some ability to suppress the extent of maximum acid swelling. This suppression is not as effective as that obtained by several of the previously discussed tanning materials, and this might be expected considering the molecular size of these vegetable tannins. Putnam and Gensler[27] have estimated the molecular weight for the main constituent of quebracho to be in the neighborhood of 600 and on this basis 0.23 gram quebracho per gram of hide substance is equivalent to 0.4 millimole tannin per gram hide substance. The observed suppression of swelling in the

acid range would indicate these tannins are combined with the amino groups of the protein.

When swelling of these tanned products was followed in the basic region, strong leaching of vegetable tannin occurred and the tannins loosely held in this region have apparently taken up water themselves adding to the water held by the protein.

It has been pointed out [28] that the vegetable tannin molecules may not be penetrating the hide powder fibers and that therefore efficient use of the relatively high tannin concentrate is not possible. However, unless penetration of the fiber has occurred, it is likely that washing would remove the greater portion of the tannin held by the hide powder. This did not occur.

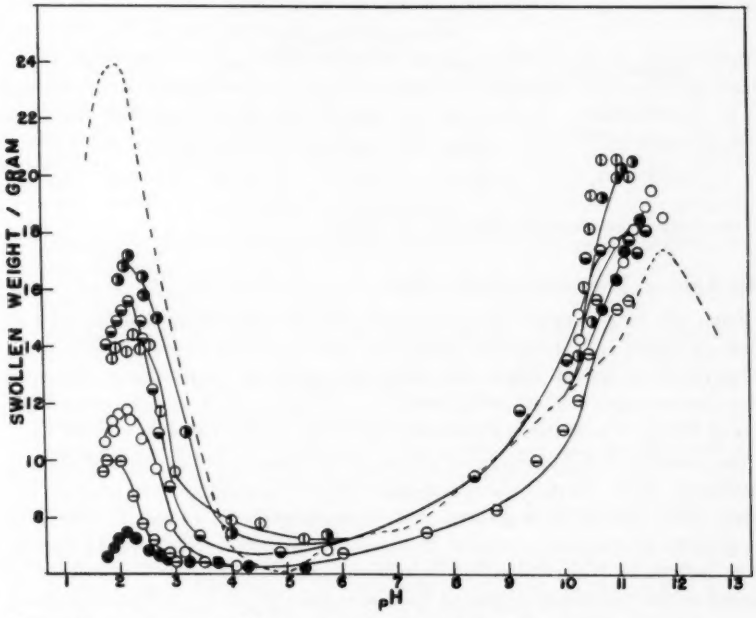

FIGURE 12. Swelling of hide powders tanned with syntans.
○ , 10 per cent syntan A; ● , 16.0 per cent syntan A; ◒ , 10.7 per cent syntan B; ⊖ , 17.0 per cent syntan B; ◑ , 14.0 per cent syntan C; ⓘ , 20.0 per cent syntanC; – – – control hide powder.

4.9 *Effect on Syntans on Swelling of Hide Powder*

The data of figure 12 correlate the swelling of hide powders tanned to contain different concentrations of three distinct syntan types. Syntans A, B, and C represent respectively, an acidic napthalene type, a sulfonated phenol-formaldehyde type, and a lignosulfonate type. Since the amounts of syntan

held by the protein are not expressible on a molar basis, no intercomparison of syntans is justified. In the concentration range shown, syntans A, and B are very effective in the suppression of swelling in acid and this would indicate these materials combine predominantly with the basic amino groups of the protein.

The results in basic region are subject to doubt since these tanning materials were drastically leached by even small quantities of alkali. The increased swelling in the strong alkaline region would indicate water take-up by the syntans themselves.

TABLE I

Effect of Temperature on Swelling

Equilibrium pH	Swollen volume (cc) per gram hide powder			Standard deviation*
	1°C	22°C	37° C	
2.05–2.15	31.4	36.8	45.0	0.5
5	13.2	14.5	13.3	0.5
11.5–11.6	22.0	24.5	27.6	0.9

*Six to eight measurements were made at each pH indicated.

4.10 *Effect of Temperature on Swelling*

From the data in table 1 it is apparent that the swelling of hide powder in aqueous media is temperature dependent and that this dependency is most pronounced in media where the Donnan equilibria and osmotic pressure forces are operative, e. g., pH 2 and 11.5. This result is in agreement with that of Porter [13] who studied the swelling of hide powder at 1°C and 24°C.

The swelling of hide powder in acid is more temperature dependent than is swelling in base. It may be noted that the swelling differential in acid between 37°C and 22°C is greater than that between 22°C and 1°C despite the greater temperature interval in the latter instance. This would appear to be indicative of factors other than pure osmotic phenomena and may be related to the increasing degree of loose structure which is predominant prior to actual solution of the protein.

In water (pH 5) the swelling is greater at 22° C than at either 1°C or 37°C. At the latter temperature three times as much protein was solubilized in twenty-four hours as was solubilized at 22°C. The maximum solution accounted for 5 per cent of the protein so that the lower swelling value at 37°C is in some degree due to loss of protein. While greater protein solution in acid or base occurred at 37°C than at the lower temperatures, the loss of measurable protein was not sufficient to nullify the increase in water take-up due to osmotic effects.

5. Summary

A detailed study has been presented of the swelling in aqueous media of collagen (hide powder) and of collagen modified by acetylation, demaination, esterification, and by tanning with different concentrations of syntans, and of aldehyde, vegetable, and mineral tanning agents. The tanning agents studied were formaldehyde, quinone, glyoxal, methyl glyoxal, chromium, zirconium, quebracho, chestnut and gambier. Measurements were made in aqueous media in which the pH was varied from 1.8 to 12.0. Some theoretical aspects of the tanning action which may occur have been discussed on the basis of the data presented.

Formaldehyde-tanned collagen is shown to be resistant to swelling in either acidic or basic media. Other tannages may suppress swelling in acid but are not as effective as formaldehyde in basic media.

The swelling of collagen in aqueous media is shown to be temperature dependent; this dependency is most pronounced in media where the Donnan equilibria and osmotic pressure forces are operative, e. g., pH 2 and 11.5. In water measurable protein swelling was greater at 22°C than at either 1° or 37°C.

References

1. Wilson, J. R., The Chemistry of Leather Manufacture, Chemical Catalog Co., New York, N. Y., 1928.
2. McLaughlin, G., and Theis, E., The Chemistry of Leather Manufacture, Rheinhold Publishing Corp., New York, N. Y., 1945.
3. Progress in Leather Science 1920-1945, British Leather Manufacturers Research Association, 1948.
4. Sookne, A., and Harris, M., *J. Research NBS* **19,** 535 (1937) RP 1043.
5. Thomas, A., and Foster, S., *J. Am. Chem. Soc.* **48,** 489 (1926).
6. Bowes, J., and Kenten, R., *Biochem. J.* **44,** 142 (1949).
7. Cassel, J., McKenna, E., and Glime, A., *J. Am. Leather Chem. Asso.* **48,** 277 (1953).
8. Fraenkel-Conrat, H., and Olcott, H., *J. Biol. Chem.* **161,** 259 (1945).
9. Gustavson, K., *J. Am. Chem. Soc.* **74,** 4608 (1952).
10. Steyermark, L., Quantitative Organic Micro Analysis, Blakiston Co., New York, N. Y., 1951.
11. Green, R., Ang, K., and Lam, K., *Biochem. J.* **54,** 181 (1953).
12. Highberger, J., and Retzsch, C., *J. Am. Leather Chem. Assoc.* **33,** 341 (1938).
13. Porter, E., *J. Int. Soc. Leather Trades Chem.* **6,** 83 (1922).
14. Proctor, H., and Wilson, J., *J. Chem. Soc. Soc.* **109,** 307 (1916).
15. Green, R., *J. Am. Chem. Soc.* **75,** 2729 (1953).
16. Fraenkel-Conrat, H., and Olcott, H., *J. Am. Chem. Soc.* **70,** 2673 (1948).
17. Bear, R., Advances in Protein Chemistry, Vol. VII, 1953.
18. Gustavson, K., *Sartryck ur Svensk Kemisk Tidskrist* **59,** 98 (1947).
19. Gustavson, K., *ibid.* **59,** 159 (1947).
20. Weir, C., and Carter, J., *J. Am. Leather Chem. Assoc.* **45,** 421 (1953).
21. Speakman, J., *J. Int. Soc. Leather Trades Chem.* **37,** 37 (1953).
22. Gustavson, K., Advances in Protein Chemistry **5,** 353 (1949).
23. Green, R., *Biochem. J.* **54,** 187 (1953).
24. Plant, D., *J. Int. Soc. Leather Trades Chem.* **36,** 351 (1952).

25. Clabaugh, W., and Gilchrist, R., *J. Am. Chem. Soc.* **74**, 2104 (1952).
26. Somerville, I., and Rau, W., *J. Am. Leather Chem. Assoc.* **44**, 784 (1949).
27. Putnam, R., and Gensler, W., *J. Am. Leather Chem. Assoc.* **46**, 613 (1951).
28. Phillips, H., Private communication.

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The Properties of Leather of Importance to the Tanner, the Shoe Manufacturer and the Wearer*

By HENRY PHILLIPS,

British Leather Manufacturers' Research Association
Milton Park, Egham, Surrey, England.

The mass production of footwear is being adjusted to the mass production of synthetic materials. This adjustment is being made to meet the demand for a greater variety of boots and shoes for specific purposes and pastimes, and the increased demand for boots and shoes in countries whose standard of living is rising. Sometimes, however, it is argued that some synthetic materials give better service than leather, and this has brought into prominence the particular properties of leather which contribute to foot comfort. The main object of this paper is to make a survey of these physical properties.

The wear resistance of most synthetic soling materials is superior to that of leather. It is therefore essential that the wear resistance of leather should be improved. Unfortunately there has been a tendency to concentrate on manufacturing properties rather than on wear resistance. A comparison of the properties of British and American sole leathers shows that this tendency is more pronounced in the United States than in Great Britain.

LEATHER AS A FIBROUS MATERIAL

Most of the unique properties of leather are due to its fibrous nature. This must be emphasized, since there is a tendency in the leather industry to pay less attention to leather fibres than the textile industries pay to textile fibers. Why have fibrous materials proved the best for our protection? Why synthesize fibers? Why not make our clothing and our boots from sheets of synthetic materials? Among the reasons often overlooked is that materials woven from fibers are strong, flexible and light in weight, properties which are not often found together in non-fibrous materials.

Fibers are strong because the long thin molecules of which they are composed lie side by side along the length of the fibre, and are not easily dragged apart. In a continuous sheet of the same substance the molecules are not orientated and the sheet tears easily. It is true, of course, that the strength

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of such a sheet depends on its thickness. But for clothing, the extent to which we can increase thickness to gain strength is limited by the density of the material. By using fibres and employing the ancient arts of spinning and weaving we get strength coupled with flexibility. In hides and skins Nature weaves the fibres in three dimensions in a manner which the textile technologists would find difficult to emulate.

Leather as a Thermal Insulator

Fibrous materials, in addition to giving us desirable mechanical properties, are good thermal insulators. The hair and wool which Nature provides to protect animals against temperature changes does so because the hair and wool entraps air and maintains it at rest. A layer of still air is a vapor conductor of heat. What evidence have we that leather protects us against changes in temperature because it is fibrous and entraps air? Such evidence is given by a comparison of the thermal conductivities of still air and various types of leather. The apparatus which has been used to measure the thermal conductivity of leathers is shown in Figure 1. [1], [3]. In this apparatus, the leather under test is placed between hot and cold plates. The cold plate is maintained at a constant temperature by water circulation. Any heat lost by the top and sides of the hotplate is counterbalanced by the heat this plate receives from the guard ring and the top plate. The heat lost by the hot plate is therefore the heat which passes through the leather to the cold plate. This is measured by the amount of electrical energy needed to maintain the temperature of the hot plate constant.

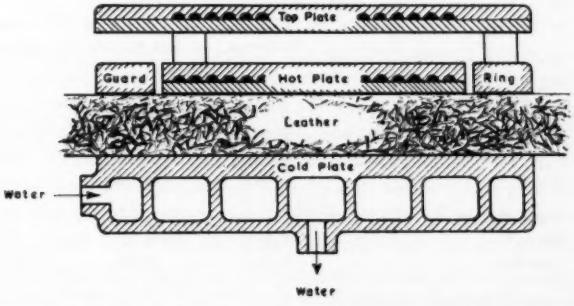

FIGURE 1. Apparatus for the measurement of thermal conductivity.

With air between the plates, the thermal conductivity is about 0.6 in c.g.s. units; in Table I the thermal conductivities of some butt, shoulder and belly leathers are given, as well as their thicknesses and bulk densities.

Note that the thermal conductivities of these leathers are about 8 to 5 times that of air. They run roughly parallel to the bulk densities, the butt

TABLE I

Thermal Conductivities and Bulk Densities of Vegetable-Tanned Sole Leathers

		I Thickness	II Bulk Density	III Thermal Conductivity
Butt	1	0.434	1.11	4.03
	2	0.565	1.13	4.44
	3	0.438	1.16	4.23
	4	0.453	1.21	4.67
Shoulder	1	0.350	1.13	3.71
	2	0.423	1.13	3.90
Belly	1	0.326	0.98	3.27
	2	0.264	0.99	2.93
	3	0.310	1.02	3.10

I, cm: II, g/cm^3: III, k x 10^4 (c.g.s. units)

leathers with bulk densities of about 1.15 having thermal conductivities about 8 times that of air, whilst the less compact belly leathers with bulk densities around 1.0 have thermal conductivities about 5 times that of air.

Table II gives the thermal conductivities of uncurried and curried vegetable-tanned upper leathers.

TABLE II

Thermal Conductivities and Bulk Densities of Vegetable-Tanned Calf Upper Leathers

		I Thickness	II Bulk Density	III Thermal Conductivity
Uncurried:				
Willow	1	0.127	0.78	1.85
	2	0.058	0.89	1.41
	3	0.097	0.70	1.94
Suede		0.075	0.64	1.84
Curried:				
Waxed		0.111	0.97	3.52
Curried		0.233	0.89	3.03

I, cm.; II, g/cm.^{3}; III, cal./cm.^{2}/sec./°C.

The uncurried leathers have thermal conductivities about 3 times that of air. Note also that their bulk densities are not much more than one half those of the sole leathers. As shown at the bottom of this table, currying with either wax or grease about doubles their normal thermal conductivities.

It is evident that the insertion of leather betwen the top and hot plates of the apparatus for measuring thermal conductivities does not greatly

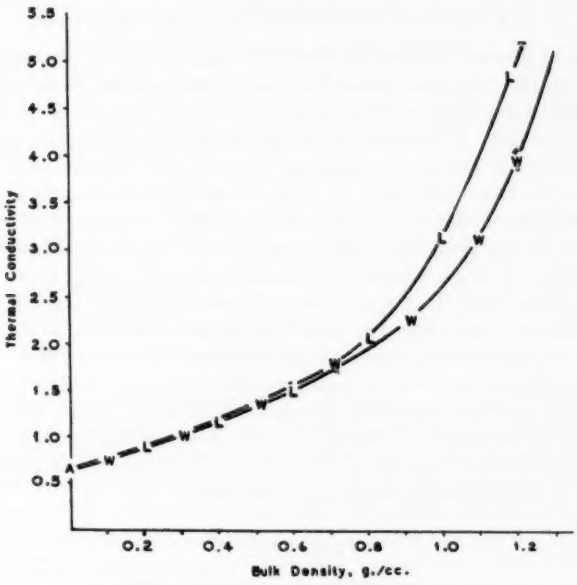

FIGURE 2. Relationship between thermal conductivity and bulk density for leather (L) and wool (W).

increase the amount of heat passing to the cold plates. As the bulk densities of the leather indicate, the light leathers contain a high proportion of air spaces. McLachlan [7], who made most of the determinations given in Tables I and II, constructed a curve relating the bulk densities and thermal conductivities of some twenty-seven leathers of all types: his curve is given in Figure 2. The second curve of this graph shows the relationship between the bulk densities and thermal conductivities of a series of wool felts measured by Baxter [1]. The thermal conductivity A for air at about 0.6 is also given. Essentially, the curves show that when the bulk density of both leather and wool felt is below about 0.5, their thermal conductivities do not greatly exceed that of air. This is not surprising, since it can be calculated that the air space in a wool felt of density 0.3 g. per c.c. is 77 per cent of the volume of the felt. Only in the more dense leathers and felts do the higher thermal conductivities of the fibres themselves exert an influence: the thermal conductivity of the wool fibre being roughly 10 times that of air, whilst the thermal conductivity of the leather fibre is somewhat higher.

From the results of such determinations it is evident that one reason why leather clothing and uppers protect the body against changes of temperature is because of the non-conducting air they contain.

The Effect of Fibre Surface on Air Movement

The air in gloves, clothing leathers and uppers cannot, however, protect the body against heat loss unless it remains more or less stationary. If the slowest gust of wind replaced the warm by cold air, then much of the protection would be lost. Fibres cannot entrap air in cells or in empty spaces in a leather. They do, however, engrap air because their surface areas are great in relation to their bulk, and air clings to solid surfaces. As Cassie [2] has pointed out, the tendency of air to cling to solid surfaces is the well-known foundation of aerodynamics, and is easily seen in the aerodynamics of a garden hedge. A hedge forms a windbreak because air clings to its branches, twigs and leaves, and the drag on the air from their large surfaces brings it to rest; in short, the hedge does not behave as a solid wall, obstructing the flow of air; it uses aerodynamic drag to slow down the rate of flow.

It is therefore of interest to compare the total fibre surfaces in various leathers; this will be influenced by the nature of the skin, the degree of splitting of the fibres into fibrils, and by the nature of the tannage. In Table III the surface areas of the fibres of tanned and untanned skins are compared with those of fine and coarse wool and natural silk.

TABLE III

Surface Areas of Leather and Wool Fibers

		ft.^{2} per lb.
I	Vegetable goat skin	5,800
	Chrome calf skin	4,600
II	Untanned hide	23,000
	Formaldehyde tanned	1,700–4,000
III	64's merino wool	800
	56's cross-bred wool	400
	Silk	3,000

I, Mitton; II, Zettlemoyer, Schweitzer, and Walker; III, Cassie.

The values for goat and calf skin were determined by Mitton [9]; they were calculated from the air permeabilities. The values for wool and silk were calculated from measurements of diameters of the fibres. The values for the untanned and formaldehyde-tanned hide were calculated from the nitrogen absorption.

Shoe Construction and Thermal Insulation

When walking, the foot is not only protected by the sole but also by the insole and the filling material between the sole and the insole. McLachlan, Goodfellow and Cushnie [8] made some measurements of these components both alone and when arranged as in a shoe. These are given in Table IV.

TABLE IV

Thermal Conductivities of Shoe Materials

		I Thickness	II Bulk Density	III Thermal Conductivity
Cork-gum bottom fillers	1	0.30	0.70	2.35
	2	0.58	0.68	2.72
Sole + cork-gum filler + insole		1.06	——	3.49
Crepe rubber....	1	0.40	0.88	3.47
	2	0.42	0.88	3.76
Composition rubber soling		0.52	1.46	8.73
Sole saturated with water		——	——	9.00

I, cm.; II, g/cm^2; III, k x 10^4 (c.g.s. units)

Note that the thermal conductivity of a cork-gum filler is relatively low, and that the conductivity of the combination sole-plus-filler-plus-insole is lower than the usual value for a sole, which is between 4.0 and 4.5.

McLachlan *et al* [8] also determined the thermal conductivity of crepe rubber. The value of 3.47 – 3.76 is very near that of leather. On the other hand, the thermal conductivity of composition rubber soling is much higher. Regarded simply as a thermal insulator between the foot and the ground, crepe rubber soling is a more serious competitor of leather than rubber composition.

The Water Vapour Permeability and the Water Absorption of Leather

Far greater importance should be attached to the water vapour permeability and water vapour absorption of leather than to the air permeability. The enormous surface area of the fibres in leather enables it to take up water vapour rapidly and to convey it to the outside air.

As an illustration of the greater importance of water vapour permeability as compared with air permeability in foot comfort, the experience of a firm that made shoes of synthetic material which were worn by members of their staff can be quoted. The uppers of the shoes were made so that their air permeabilities were similar to those of upper leathers. Yet one of the staff, who undoubtedly had very sweaty feet, complained that towards the end of a warm day he could pour sweat out of his experimental shoes.

These shoes, besides having synthetic uppers, also had synthetic soles. In Table V the water vapour permeabilities of some vegetable-tanned sole leathers are compared with those of Neolite and polyvinyl sheet and polyvinyl-coated fabrics.

The water vapour permeabilities of the sole leathers are relatively low compared with those of upper leathers. People wearing shoes soled with leather seldom pour sweat out of their shoes, because although leather soles

TABLE V

The Water Vapour Permeabilities of Sole Leathers

		Thickness cm.	Permeability mg./cm.²/hr.
Vegetable	1	0.47	5.0†
	2	—	1.9*
	3	—	2.0*
	4	—	2.0*
Neolite			0.0*
Polyvinyl sheet			0.1†
Polyvinyl-coated fabric			0.6†

†G, 100% R. H.; F, 0% R. H.\
*G, 70% R. H.; F, 0% R. H./ Mitton

may not transmit water vapour very quickly, they can and do *absorb* water vapour. The amount they can absorb without becoming wet is considerable.

The synthetics, Neolite, polyvinyl sheet and coated fabric, do not absorb moisture, and, as shown in Table V, their water vapour permeabilities are very small. According to Mitton[10], the values quoted for the polyvinyl sheet and fabric are probably too high, because very small leakages, which would cause a large error, may have occurred around the edges of the test specimens.

Whilst sole leathers may transmit 2–5mg. per sq.cm. per hour, upper leathers, as shown in Table VI, will transmit about four times this amount. Probably the grease content of the heavy chrome upper leather was responsible for the lower permeability.

TABLE VI

The Water Vapour Permeabilities of Upper Leathers

	Thickness cm.	Permeability mg./cm.²/hr.
Chrome calf skin	0.09	19.1
Chrome goat skin	0.12	11.4
Vegetable sheep skin	0.13	14.9
Heavy chrome upper	0.25	8.1

The transmission of water vapour is favoured because, unlike air, it is transmitted by and through the substance of leather fibres themselves. Although no measurements appear to have been made on leather fibres, Cassie[2] showed that suitably exposed wool fibres reach equilibrium with a moist atmosphere in about 2 seconds. The absorption is very rapid because the surface area of the fibres is so great and because water vapour travels quickly inside the fibre. The amount of water vapour leather will absorb is

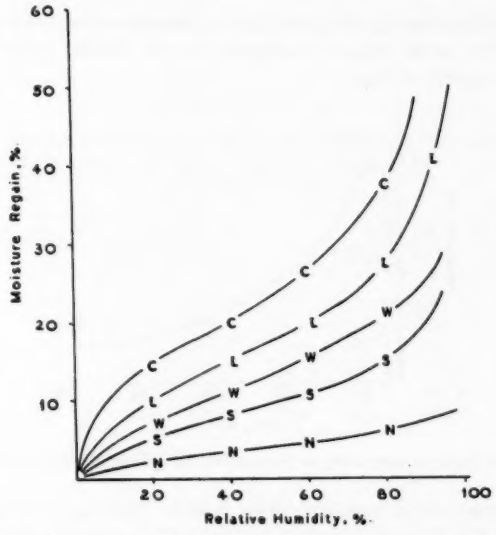

FIGURE 3. The water vapour absorptions of chrome and vegetable leathers (C) chrome leather; (L) vegetable leather (W) wool; (S) silk; (N) nylon.

dependent on the relative humidity of the air. Figure 3 shows the relation between relative humidity and the regain of vegetable and chrome leathers: that is, the moisture content calculated as a percentage of the weight of the water-free leather. These are regains of moist leathers after they have reached equilibrium with air of different relative humidities. The L curve is the relative humidity/regain curve for vegetable-tanned leather: it is lower than the curve C for chrome leather.

For purposes of comparison similar curves for wool, silk and nylon are included. It is interesting that at any given relative humidity the regain of leather exceeds that of the three textile fibers.

The greater water vapour absorption of chrome leather as compared with that of vegetable-tanned leather is noteworthy. The curve for chrome leather is very similar in shape and at the same level as the curve obtained by Kanagy [4] relating the water vapour absorptions of hide powder with relative humidity.

The Thermostatic Properties of Leather

The importance of the ability of leather to absorb and transmit water vapour is not confined to the removal of perspiration. When damp leather loses moisture and comes to equilibrium with air of low relative humidity it becomes colder. This is because it supplies heat to the moisture, and this is carried away as kinetic energy by the water vapour into which the moisture

is converted. Conversely, when dry leather absorbs water vapour, it becomes warm: when the water vapour condenses on the leather substance, it gives up its kinetic energy as heat.

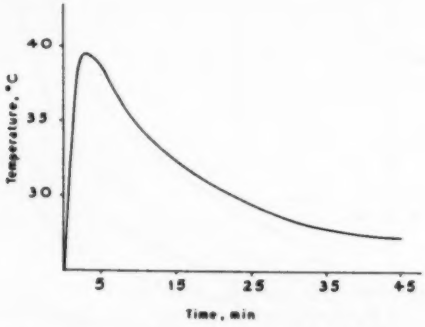

FIGURE 4. The rise in temperature of chrome leather during absorption of water vapour.

Let us consider what happens when leather clothing or shoes are taken on a winter's day from the warm, dry air of a heated and well-ventilated room to the cold, damp air outdoors. Whilst indoors, the leather came into equilibrium with air of low relative humidity and its regain fell. Outdoors, the relative humidity is high, and the leather begins to absorb water vapour, which gives up heat, and this raises the temperature of the air penetrating through the leather. The magnitude of this heat of absorption of water vapour by leather is appreciable: Lykof[6] dried some chrome leather shavings and put them, together with a thermo-couple, in a glass tube, through which he then passed moist air at 25°C. The alteration in the temperature of the chrome leather shavings Lykof recorded are given in Figure 4. Note that the temperature of the leather rose from 25° to a maximum of 39°C. in about two minutes. It was then slowly cooled by the air passing through, but even after 40 minutes its temperature exceeded 25°C.

Although these laboratory measurements and experiments reveal the thermostatic properties of leather, there appears to be very little information concerning the changes in the moisture content of shoes during wear. Many questions remain to be answered. Is foot perspiration, for example, lost very rapidly? Does a leather sole help to remove perspiration, or is it no better than an impervious soling material? What part does the sock play in absorbing perspiration? In an attempt to obtain some information bearing on these questions, pairs of shoes were worn made up of one leather-soled and one Neolite-soled shoe, but otherwise identical. In the first test on two pairs of these shoes each pair was worn on alternate days near London in January, 1951, and was weighed immediately on returning home in the evening, and again after being kept in a cool room and before being put on

again 36 hours later. The changes in the weights of these shoes during the test are given in Table VII.

TABLE VII

Shoes: Changes in Weight of Leather—and Neolite-Soled Shoes Caused By Alterations in Moisture Content During Wear
Weights in Grams

	Pair A					Pair B			
	Leather		Neolite			Leather		Neolite	
	Morn.	Eve.	Morn.	Eve.		Morn.	Eve.	Morn.	Eve.
Sat.*	—†	515.5	——	534.1	Sat.	——	497.1	——	522.4
Sun.	——	516.3	——	534.6	Sun.	——	502.7	——	526.7
Mon.	516.3	519.0	534.7	533.7	Tues.	503.4	523.1	526.6	536.3
Wed.	521.4	530.2	536.7	537.8	Thur.	519.5	525.6	536.3	537.6
Fri.	528.2	529.0	538.1	538.1	Sat.	522.8	521.1	538.1	539.0
Sun.	——	528.2	——	540.2	Sun.	——	520.4	——	538.7

*13th January, 1951. †Indicates not worn.

Note that during the week's wear each pair of shoes gained steadily in weight, the wholly leather shoe gaining more weight than the Neolite-soled shoe. For example, with Pair A the gain in weight from Monday morning until Friday evening was 12.7g. for the leather-soled shoe and 3.4g. for the Neolite-soled shoe, with Pair B the gains from Tuesday morning to Saturday night were, respectively, 17.5g. and 12.4g.

This test shows that in spite of the shoes resting between each day's wear they did not lose the moisture they gained during wear, and as a result their moisture contents, steadily increased. This moisture is not all perspiration,

TABLE VIII

Changes in Weight of Leather—And Neolite-Soled Shoes Casued By Alterations in Moisture Content During Outdoor and Indoor Wear

	Pair A					Pair B			
	Leather		Neolite			Leather		Neolite	
*Date	Morn.	Night	Morn.	Night	Date	Morn.	Night	Morn.	Night
5	524.6	516.9	538.5	532.6	6	515.0	514.1	536.2	535.6
7	518.5	523.4	534.1	536.4	8	514.6	510.8	536.7	536.4
9	524.0	517.4	537.9	534.5	10	513.0	502.1	537.4	531.5
11	520.1	517.1	536.5	535.3	12	510.0	506.7	536.6	533.1
13	519.4	516.9	536.5	535.5	14	509.9	505.7	536.5	534.4
15	517.4	514.0	535.3	534.2	16	506.3	525.5	535.6	542.8
17	514.4	517.4	536.1	535.0	19	——	——	——	——
20	516.5	512.6	534.7	531.4	19	516.7	510.3	538.1	535.9
22	513.3	510.9	532.0	529.0	21	511.4	503.4	536.7	533.8
24	512.5	520.7	530.7	534.3	23	504.8	502.7	532.3	533.8

*February, 1951

since the major increases in weight took place when the shoes were worn on a wet day.

In a second test, the shoes were not taken off immediately on returning home, but were worn for some hours in a warm room. As shown in Table VIII, under these conditions of wear the shoes did not steadily increase in weight, but when worn indoors lost so much moisture that they frequently absorbed moisture when left in the cool room for 36 hours. In fact, it is possible to deduce from these figures when the shoes were worn for some hours indoors, and whether it was raining when the wearer returned home. The leather- and Neolite-soled behave similarly, except that the leather sole makes the shoe much more responsive to conditions of wear: it doubles the uptake of moisture and hence doubles the thermostatic powers of the shoe.

Whilst such tests show that a leather sole, unlike the resin-rubber material, absorbs and loses moisture according to outside conditions, they give no evidence that it plays any part in helping to remove perspiration. It would appear that during these tests most of the perspiration passed through the uppers or was absorbed by the insoles, the gains in weight being mostly caused by the absorption of rainwater. This is indicated by the weights before and after wear of the socks worn during the first test. The socks, rather unexpectedly, increased in weight during each period of wear, as shown in Table IX.

TABLE IX

Socks: Loss of Moisture During Wear

	Leather Soles			Neolite Soles		
	Morning	Evening	Difference	Morning	Evening	Difference
*Monday	32.7	32.2	−0.5	32.1	31.6	−0.5
Tuesday	32.7	32.5	−0.2	31.7	31.6	−0.1
Wednes.	33.5	33.0	−0.5	32.6	31.8	−0.8
Thurs.	33.7	33.0	−0.7	32.2	32.1	−0.1
Friday	32.2	33.3	+0.1	32.3	32.1	−0.2
Satur.	33.8	33.2	−0.6	32.9	32.3	−0.6
Sunday	33.5			32.5		

*5th January, 1951

The losses in weight when worn with shoes with leather and with Neolite soles were the same. The explanation of this loss is that the socks were maintained during wear at 98.4°F., or blood heat, by the feet. At this temperature they cannot hold as much moisture as they can when exposed to the air of a cool bedroom at 50-54°F.

It was thought that further information could be obtained by the examination of the insoles of the shoes. Changes in the analyses of the insoles might reveal differences in the conditions within the shoes depending on whether

they were soled with leather or with an impermeable soling material. This would appear to be likely when we consider the available evidence on the amount of perspiration given off by the feet.

Kuno [5] has shown that from the palms of the hands and the soles of the feet perspiration is five to ten times as great as from the general body surface. He has also provided evidence that sweat is secreted continuously by the very large number of sweat glands on the palms of the hands and the soles of the feet. It would appear that the sweating of hands and feet is partly a means of keeping the skin supple. Mitton [10] has shown that the average rate of perspiration on the whole foot when at rest is about 6 to 7mg. per sq. cm. per hour. From a man's foot of 550 sq. cm. surface area this gives a total of 39.6g. of perspiration per twelve-hour day for the lower rate of 6mg. per sq. cm. per hour. On a warm day with moderate exercise this rate is more than doubled.

The Boot and Shoe Research Association supplied postmen with pairs of boots, one of which was soled with leather and one with composition rubber. The boots were worn for from 1,000 to 1,500 miles during the cool, cold and wet weather extending from October to April. They obtained analytical evidence that the leather insoles of the two boots were changed to different degrees: the insole of the rubber-soled boot being more seriously affected by perspiration than the insole of the leather-soled boot. Table X gives the average differences in the analyses of the insoles from three pairs of these boots.

TABLE X

Average Differences in Analyses of Insoles Before and After Wear in Shoes with Leather and With Rubber Outsoles

	Leather outsole	Rubber outsole
Moisture	+1.4	+1.4
Grease	−2.2	−2.0
Total water-solubles	−1.9	−5.2
Ashed insolubles	+0.1	+0.1
Hide substance	+0.8	+1.0
Fixed tan	−2.9	−1.3
Total	−4.7	−5.4
Ashed water-solubles	−0.2	−0.6

Differences are calculated as % weight of new insole.

The samples for analysis were taken from the heel, tread and toe. The loss of water solubles and total ashed solubles was higher from the rubber- than from the leather- soled boot. Although in Table X average differences for the insoles of three pairs of boots are given, the difference between the insoles of each pair varied in the same direction. In addition, the insoles

from the rubber-soled boots all lost more weight during wear than the insoles from the leather-soled boots, and were also reported as being somewhat darker in colour.

The suggested explanation of these differences is that perspriation passes quickly through the insole of the leather-soled boot and dissolves only a small amount of soluble matter. Impermeable rubber soles, on the other hand, cause foot perspiration to be retained longer in the insoles, so that there is more opportunity for extraction of solubles, which are absorbed by the socks and migrate to the linings and uppers.

The opinion is often expressed that a leather sole cannot absorb perspiration because it is insulated from the insole by impervious fillers. It is of interest, therefore, that all these boots were constructed with tarred felt as bottom filler, but in spite of this the leather sole did influence the conditions within the boot.

The Wearing Properties of American and British Sole Leathers

Thermal insulation and power to transmit and absorb moisture accompanied by thermostatic action are valuable benefits derived from the use of leather. Because of these characteristics, coupled with its strength, leather for uppers, has few, if any, rivals. But sole leather must show another important characteristic—it must show resistance to wear.

Any consideration of wear must be linked with dimensional stability during wear. In fact, unless a soling material is dimensionally stable, its useful life is limited. A material with great wear resistance which nevertheless bulges under the stress applied by the foot can ultimately give a sole which is far from flat and is therefore uncomfortable. Further, as it spreads it may cause distortion of the whole shoe. The lack of great wear resistance by a leather or other material which is not perfectly stable may therefore be an advantage, in that wear removes the uncomfortable bulges which may arise. We are all familiar with the man who wears round holes in the soles of his shoes; when he wears highly wear-resistant soles, instead of holes bulges may appear where his foot applies local pressure.

One of the reasons why leather soles give comfort is because a compromise is made between dimensional stability and resistance to wear. Nevertheless, it is idle to conclude that we can afford to ignore the lack of wear resistance of leather in comparison with its competitors.

In the leather industries of many countries there has been a tendency to modify the characteristics of leather to provide the shoe manufacturer with leather which will give him the minimum of trouble as it passes through his factory. This is particularly true of sole leather. An American sole leather tanner has been reported as saying to a British tanner: "One of the chief differences between your aims and ours seems to be that we are out every time to suit our customers, while you British tanners seem to make leathers

to suit yourselves and to let your customers find out for themselves how to use them. No two of your sole leathers are alike, but you can go to tannery after tannery in our country and find leathers which are as alike as two peas."

The customer the American tanner had in mind was the shoe manufacturer. Has this insistence on a "manufacturers' " leather led to the production of bottom leather with poor wear resistance? Has the production of British sole leather followed more conservative lines because a greater proportion of British production reaches the public through the shoe repairer?

Periodically in the past these questions have assumed importance, and at intervals through the years the B.L.M.R.A. has made comparisons between American and British bottom leathers. In 1952 twelve bends typical of American production were received from Dr. O'Flaherty, and twelve samples of British bends were despatched to him. It is of interest to compare the results of the B.L.M.R.A. examination of these 1952 leathers with those given by American and British leathers in 1937 and again in 1939.

The first batch of American leathers examined in the B.L.M.R.A. laboratories in 1937 were described as "cut soles of unknown sampling position". They were compared with a set of British leathers supplied by members of the B.L.M.R.A. from prime parts of their manufacturing bends. The second batch of leathers to be examined were collected in 1939. The leathers were all sole bands and included seven American and five British leathers. It was intended to use these leathers to compare the abrasion machines used in various European countries, but owing to the outbreak of war this was abandoned, but a general examination of the leathers was made. The 1952 leathers which have been examined are possibly the most representative set of leathers of each country's production that the B.L.M.R.A. have had.

In Great Britain some reliance is placed on the microscopical assessment of leathers. In Table XI are arranged the assessments of the three batches of American leathers and those of the British leathers with which they were compared.

TABLE XI

Microscopical Assessments of American (A) and British (B) Sole Leathers

	1937		1939		1952	
	A	B	A	B	A	B
Boldness	4.7	5.3	—	—	4.4	5.2
Orderliness	5.0	3.9	—	—	4.7	5.5
Angle of Weave	7.0	5.3	—	—	7.1	5.6
Compactness	5.6	6.0	—	—	4.8	6.0
Fullness	5.4	5.4	—	—	5.3	6.0
Straightness	6.0	6.0	—	—	4.9	4.8
Non-splitting	1.3	2.1	—	—	1.9	4.6
Non-separation	4.6	5.6	—	—	4.2	6.2
Microscopical assessment	5.7	5.7	4.0	5.8	5.3	6.3

For the 1937 leathers, the assessments are the averages of those given by seven samples. By this rather rough and ready method of comparison, there is not much difference in the assessments for the American and British leathers, except that the fibres of the British leathers are less split up—the assessment for non-splitting is higher—and there is less separation of fibres and fibrils. In addition, the angle of weave of the American leathers tends to be higher than that of the British leathers. Unfortunately only the general assessments of the 1939 leathers are available, and the averages of these are given in the Table. In the B.L.M.R.A. records there is no mention of any particular factor in the choice of samples to account for the relatively low general microscopical assessment of this batch of American leathers.

The assessments for the 1952 batches are more complete. Again, the British leathers are given a higher general assessment—6.3 against 5.3—and again the main difference shown is the higher assessment gained by the British leathers for non-splitting and non-separation, and the higher angle of weave of the American leathers.

FIGURE 5. Fibrous structure of American sole leather.

The difference in microstructure is clearly shown in Figures 5 and 6. These photomicrographs show the extremes encountered in the microscopical examination. The fibres of the American leather in Figures 5 are much more split and separated than are the fibres of the British leather (Figure 6). This difference can be illustrated by reference to Figure 7. The state of the fibre bundles in the British leathers is somewhere between A and C, being nearer

FIGURE 6. Fibrous structure of British sole leather.

to A than to C. On the other hand, the fibre bundles of the American leathers are somewhere between B and D, being nearer to B to to D.

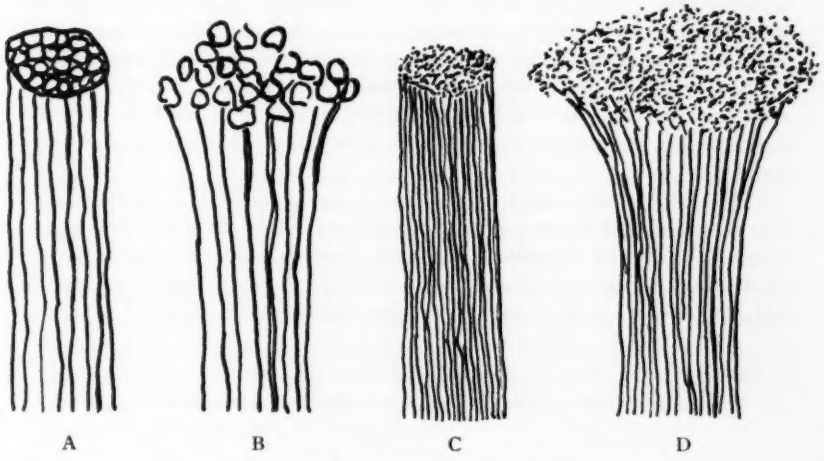

FIGURE 7. A, Fibre bundle split into fibres which have not separated.
B, Fibre bundle split into fibres which have separated.
C, Fibre bundle split into fibrils which have not separated.
D, Fibre bundle split into fibrils which have separated.

The information on the physical properties of all six batches of leathers is more complete, and is gathered together in Table XII. The figures for the rates of abrasion of the 1937 leathers are not available, but those for the 1939 and for the 1952 leathers both show that on average the rates of abrasion of the British leathers are lower than those of the American leathers.

TABLE XII

Physical Properties of American (A) and British (B) Sole Leathers in 1937 1939 and 1952

		1937		1939		1952	
		A	B	A	B	A	B
Rate of abrasion	Corium	—	—	0.29	0.20	0.200	0.184
	Whole thickness	—	—	0.33	0.26	0.266	0.247
Q 15		21	16	16.9	15.9	20.0	12.8
Q 24		24	22	23.7	21.2	27.2	23.9
Loss on soaking		12	10	10.1	5.8	14.6	8.4
Free Water		36	32	33.8	27.0	41.7	32.3
Apparent density	Before Soaking	1.09	1.14	1.04	1.08	1.04	1.08
	After soaking	1.01	1.03	0.93	1.03	0.92	1.01

The outstanding differences between the leathers is, however, the difference in their behaviour towards water. The resistance of British leathers towards water has apparently always been better than that of American leathers. Q15, the water absorbed during 15 minutes' immersion, has always been lower, as has also Q24, the water absorbed during 24 hours' immersion. The loss on soaking is also consistently lower. The "Free Water" figures of the British leathers, which are a measure of the free space in the leathers after the Q24 test, are also lower. For this reason, the British leathers are consistently more dense both before and after soaking than are the American leathers.

Taking all the data into consideration, it is evident that the properties of present-day British leathers do not differ greatly from those of leathers produced in 1937. On the other hand, there may be signs that the American leathers are not so good as they were in 1937: they give higher values for Q24, lose more on soaking, and give higher values for "free water".

TABLE XIII

Average Analyses of American (A) and British (B) Sole Leathers in 1937 and 1952

	1937		1952	
	A	B	A	B
Water solubles	58	74	60	58
Degree of Tannage	78	74	76	70

It is curious that whilst the microscopical assessment of the leathers differ, and their physical properties are not the same, yet their analyses are very much the same. No analyses of the 1939 leathers are available, but in Table XIII are recorded the average figures for the water-solubles and degrees of tannage of the 1937 and 1952 batches of leathers.

On this evidence there appear to be no essential differences in the analyses of American and British leathers: their Degrees of Tannage are very much the same, and whilst in 1937 the British leathers had the higher water solubles, they had the lower solubles in 1952.

The splitting and separation of the fibres which is a characteristic of American production can be attributed to tanning treatments in drums. British tanners do not give their sole leather nearly as much drumming. Splitting and separation of fibres lowers the density of the leather. This is the most consistent difference between American and British leathers. From the tanning standpoint, as shown by the Degrees of Tannage, the fibrils of American leathers are tanned to roughly the same degree as the fibres of British leathers. American leathers are therefore less dense than British leathers, because they have a smaller weight of fibrils and fibres per unit of volume.

We have made many observations which indicate that leathers which absorb water freely and have high Q24 values abrade quickly and do not wear well. The desire of the British tanner to produce a compact leather with a low Q24 figure and also with a low loss on soaking arises from his wish to produce a waterproof leather with good wearing properties when wet. The American tanner, on the other hand, may have sacrificed wet wear resistance to ensure that he provides the shoe manufacturer with a leather which is easily worked.

Conclusions

To summarise, there should be a greater appreciation of those benefits, besides strength, flexibility and low density, which follow from the fibrous nature of leather—thermal insulation, water vapour permeability and absorption which enable leather to absorb and transmit perspiration from the foot whilst guarding it against abrupt changes in temperature.

In comparison with its competitors, only the wear resistance of sole leather gives rise to anxiety. Our survey suggests that the desire to satisfy manufacturing requirements may be leading to the production of sole leather with inadequate wear resistance particularly in wet weather. A comparison of American and British sole leathers suggests that this tendency is more pronounced in America than in Great Britain.

Bibliography

1. Baxter, S., *Proc. Phys. Soc.* (*London*), **58**, 105 (1946).
2. Cassie, A. B. D., *J. Text . Inst.* (*Manchester*), **40**, 444P (1949).

3. Hercus, E. L., and Laby, T. H., *Proc. Roy. Soc.* (*London*), A **95,** 190. (1919).
4. Kanagy, J. R., *J. Am. Leather Chemists Assoc.*, **42,** 98, (1947).
5. Kuno, Y., *The Physiology of Human Perspiration*, 1934. J. & A. Churchill, London.
6. Lykof, A. W., *Kolloidzschr.*, **71,** 333 (1935).
7. McLachlan, N. W., *J. Soc. Leather Trades' Chemists*, **26,** 135 (1942).
8. McLachlan, N. W., Goodfellow, H., and Cushnie, H. C., *J. Soc. Leather Trades' Chemists*, **26,** 23 (1942).
9. Mitton, R. G., *J. Soc. Leather Trades' Chemists*, **29,** 262 (1945).
10. Mitton, R. G., *J. Soc. Leather Trades' Chemists*, **31,** 44 (1947).
11. Zettlemoyer, A. C., Schweitzer, E. D., and Walker, W. C., *J. Am. Leather Chemists Assoc.*, **41,** 253 (1946).

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ABSTRACTS

The Measurement of Real Volumes of Leather by Gas Displacement. R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **38,** 2 (1954). Measurement of real volumes of collagen fibers and leather, published by the author and coworker *J.S.L.T.C.* **35,** 360 (1951) and *This Journal*, **47,** 439 (1952), gives results which do not agree with those obtained by Spiers *J.S.L.T.C.*, **36,** 20 (1952), in spite of the fact that in both cases measurement was made by gas displacement. It was further noteworthy that each set of data was consistent in itself, giving results reproductible to less than one per cent, while the two sets varied from each other up to fifteen per cent. Spiers' measurements, obtained with a volumenometer of his own design, were lower. For a further study the author built a modified volumenometer and made measurements of the real volumes of commercial hide powder, acetone dehydrated ox cheek hide, chamois leather and several samples of chrome and vegetable tanned leather. The results obtained were in good agreement with the results previously obtained by the author. The experiments showed that the lower results obtained by Spiers were not caused by a different method of preparing samples. R. H. T.

Report of the Committee for Determination of Copper and Iron in Vegetable Tanning Extracts. G. Forsyth. *J. Soc. Leather Trades' Chemists*, **38,** 8 (1954). A provisional method for the determination of iron colorimetrically is given in detail.—R. H. T.

The Constitution of Sulfated Oils. VI. Effects of Variations in the Method of Manufacture on the Composition of Sulfated Fish Oil. D. Burton and L. F. Byrne. *J. Soc. Leather Trades' Chemists*, **38,** 10 (1954). A brief review of the literature on the subject is given. To study the effects of varying conditions in sulfating fish oil, fourteen variations were made giving fourteen different oils. Oil I. 5 per cent sulfuric acid for 5 hr. at 20° washed with 20 per cent ammonium sulfate at 20°, neutralized with ammonia at 20°, neutralized with ammonia at 20°. Oils II, III, IV, V and VII were treated with 20 per cent sulfuric acid for 5 hr., oils II and VII at 20°, oils IV and V at 27° and oil VI at 40°. Oils II through V were washed with 20 per cent NaCl at 20° and oil VII with 20 per cent ammonium sulfate at 20°. Oils II, IV and VI were neutralized with caustic soda at 20°, while III, V and VII were neutralized with ammonia at 20°. In the remaining variations all oils were neutralized with caustic soda at 20°C. and all washing with NaCl at 20°, except oils XII and XIII, which were washed at 40° and all treatments were at 20° except

XII and XIII, which were treated at 5°. Oil VIII, treatment 60 per cent sulfuric acid for 7 hr., washed with 20 per cent NaCl and neutralized with caustic soda. Oil IX, treatment 100 per cent sulfuric acid plus 25 per cent flacial acetic acid for 7 hr., washed with 20 per cent NaCl and neutralized with caustic soda. Oil X, treatment 50 per cent oleum (20 per cent) for 6 hr., washed with 20 per cent NaCl and neutralized with caustic soda. Oil XI, treatment 50 per cent oleum (20 per cent) plus 25 per cent acetic anhydride for 6 hr., washed with 20 per cent NaCl and neutralized with caustic soda. Oil XII, treatment 100 per cent oleum (20 per cent) plus 50 per cent benzene for 10 hr., washed with 20 per cent NaCl and neutralized with caustic soda. Oil XIII, treatment 100 per cent oleum (20 per cent) plus 25 per cent glacial acetic plus 25 per cent benzene for 10 hr., washed with 20 per cent NaCl and neutralized with caustic soda. Oil XIV, treatment 39 per cent chlorsulfonic acid plus 20 per cent glacial acetic for 6 hr., washed with 20 per cent ammonium chloride and neutralized with ammonia. The analyses of all 14 oils are given. The conclusions are: (1) Raising the temperature of the reaction from 20 to 40 degrees, when the fish oil is being treated with 20 per cent of its weight of sulfuric acid, has little effect on the extent of hydrolysis of the glycerides, or the amount of sulfuric ester, or the formation of hydroxy-fatty acids and their derivatives. A translucent oil containing no sulfonates is formed at 40°, while a clear oil containing an appreciable amount of sulfonate is formed at 20°. (2) Increasing the proportion of sulfuric acid from 20 to 60 per cent increases the degree of hydrolysis of the glycerides from 21 to 69 per cent and the sulfonate formation nearly threefold. The sulfuric ester content does not vary greatly, but the free and neutralized hydroxy-fatty acids are doubled in amount. The viscosity of the oils increases. (3) The hydrolysis of the glycerides is greater when 100 parts of the fish oil are treated with 100 parts of sulfuric acid and 25 parts of glacial acetic acid at 20° than when 100 parts are treated with 39 parts of chlorsulfonic acid and 20 parts of glacial acetic acid at 20°. (4) The sulfuric ester formation is greatest when 60 parts of sulfuric acid at 20° is used and least when 100 parts of 20 per cent oleum, 25 parts of glacial acetic and 25 parts of benzene are used at 5°. (5) The sulfonate formation is greatest when 100 parts of sulfuric acid and 25 parts of glacial acetic acid are used at 20°, and zero with 39 parts of chlorsulfonic acid and 20 parts of glacial acetic at 20°. (6) The formation of hydroxy-fatty acids and their derivatives is greatest by using 100 parts of 20 per cent oleum, 25 parts of glacial acetic acid and 25 parts of benzene at 5°; and least by using 39 parts of chlorsulfonic acid and 20 parts of glacial acetic at 20°. (7) Neutralizing with ammonia instead of caustic soda has practically no effect on the hydrolysis of glycerides, the amount of sulfuric ester or the amount of sulfonate formed. (8) The fall in iodine value is not an indication of the amount of sulfuric ester and/or sulfonate formation: and there is no significance in any so-called degree of sulfation figures calculated from the fall in iodine value. (9) The ability to form a solution instead of an emulsion is not, as commonly stated, a function of sulfuric ester and/or sulfonate content of sulfated oil. (10) It should be noted that the sulfated oils were allowed to stand in the acid condition over night before being neutralized. This has probably given rise to the formation of free fatty acids by hydrolysis of the glycerides. R. H. T.

Particle Size Determinations of Leather Finishing Agents. E. Atherton and R. H. Peters. *J. Soc. Leather Trades' Chemists*, **38**, 22 (1954). One of the most important physical properties of aqueous dispersions used in leather finishes is the size of the particles composing the dispersion. A very rapid method for measuring particle size is available for those dispersions whose particles are spherical in shape and whose particle size lies in the range of 0.05 to 0.30 *mu*. The method is based on the light scattering properties of such systems. A complete description and discussion of the method for measuring particle size of leather finishes is given. It is easy to use and suitable for routine determinations. The

instruments required are a refractometer and an absorptiometer capable of turbidity measurement. It is demonstrated that additional measurements of disymmetry, to allow for interference effects on the measured turbidity, are unnecessary and that a calibration curve may be drawn relating particle size to concentration and turbidity as measuerd. In determining particle size by means of turbidimetric measurements it is necessary, in general, to make a correction for the interference effects in the scattering envelope arising from the finite size of the particles. The dissymmetry ratio is found to bear a unique relation to the particle size and the decrease in turbidity due to interference. Hence it is possible to make the correction from a knowledge of this ratio. Unfortunately measurements of the latter must, in general, be made in an instrument other than that used for the measurement of turbidity. It has been shown in this work that, for systems of spherical particles, this may be avoided and a relation between the experimentally measured turbidity and particle size has been derived. It is therefore possible to obtain measurements of particle size from turbidity alone, and the relation has been given in the form of a graph. In addition it is necessary to determine the slope of the refractive index/concentration curve; but, since for a given polymer this appears to be independent of particle size, it need only be determined once for each system studied. R. H. T.

The Evaluation and Control of Leather Finishes. J. S. Mudd. *J. Soc. Leather Trades' Chemists*, **37**, 44 (1954). Evaluation of finishes is still more often made by the skill of the operator than by technical tests. In this paper a number of tests are presented and described. *Specific gravity*. Any established method suitable for heavy, viscous liquids is satisfactory. Where quantities are available it is suggested that the determination can be made rapidly with sufficient accuracy by weighing in a large graduated cylinder. *pH*. The glass electrode method is recommended. Colorimetric determinations cannot be made. *Color*. While at very low luminance a colorimeter may not be as sensitive as the human eye, in general colorimeter measurements are most advantageous. Details of the method were published *J.S.L.T.C.*, **37**, 353 (1953) and *This Journal*, **49**, 454 (1954). *Relative opacity*. This determination is an essential routine test. An electronic method was described *J.S.L.T.C.*, **37**, 67 (1953). *Viscosity*. Only the rotational viscosimeters of the coaxial cylinder type are suitable. The materials are nearly always non-Newtonian and viscosity measurements are meaningless unless accompanied by the rate of shear at which the determination is made. Use of the Ferranti portable viscosimteer is described. The instrument covers a range of 0-1250 centipoises and a shear rate range of 3-530 reciprocal seconds. In addition to the preceding routine tests, several occasional tests such as total solids, ash value, organic pigments by elutriation and examination of metals follow normal textbook practice. Of the purely practical tests hot pressing, glazing and ironing are the most important. The assessment of fading is becoming increasingly important. R. H. T.

On the Reaction Between Chemically Modified Collagen and Some Chrome Tanning Complexes. R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **38**, 51 (1954). The modified collagens used are listed in the following Table:

Treatment	Side-chain Carboxyl (Expressed as m moles/g. protein)	Side-chain Amino (Expressed as m moles/g. protein)
None	1.00	0.34
Nitrous acid	1.05	0.07
Dinitrofluorobenzene	1.00	0.08
Sodium glyoxalate	1.19	0.14
Sodium bromoacetate	1.56	0.07
Methyl sulfate (i)	0.58	—

Methyl sulfate (ii)	0.28	0.07
Acid catalysed methanol	0.14	0.34
Acid catalysed methanol on deaminised collagen	0.18	—
Lithium aluminum hydride	0.43	—

These modified collagens were tanned in both cationic and anionic chrome liquors over a pH range of about 2.5 to 4.3 for the cationic and about 2 to 7 for the anionic. An attempt was made to relate the up-take of chromium to the composition of the tanning liquor. Data are given covering the final pH, the per cent Cr_2O_3 content and the shrinkage temperature of the leathers, for both the cationic and anionic tannages. A figure constructed from the data obtained with the cationic tannage shows that there is a linear relationship between the logarithm of the chromium oxide content and the shrinkage temperature of the leather and this appears to be independent of any pretreatment of the collagen prior to tanning. Carboxylation of collagen increased the amount of chromium fixed and raised the shrinkage temperature. In carboxylating collagen nearly all the free amino groups were blocked by the carboxylating agent. The results therefore indicate that the amino groups are not essential for chromium fixation or hydrothermal stability. Both the esterified and alkylated collagens yielded products which were not leather in the accepted sense. It is obvious from the data that there is no direct relationship between the amount of chromium fixed and the total number of carboxyls in the collagens. It is apparent that, during tannage, the amino groups play no direct part in the fixation of chromium but only an indirect one through their effect on the number of carboxyl groups which will be ionized at a given pH. R.H.T.

Structures of Basic Chromium Sulfate Complexes. S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists,* **38,** 58 (1954). Work of other investigators is briefly reviewed and discussed. Experimental study of the effects of adding potassium sulfate on the degree of olation of basic and non-basic chromium nitrate solutions, the effects of sulfate additions on the coordination of sulfate groups to chromium, and the effects of addition of sulfate at the boil on 120 and 8 g./l. chromium nitrate complexes were studied. Structure for 66 per cent and 33 per cent basic chromium nitrate are suggested with changes on treatment with sulfate. Also suggested are a series of ring structures of varying stability. The author makes the following factual observations. If sufficient alkali is not present to convert all the chromium molecules of a chromium nitrate solution to diol complexes, the addition of sulfate ions enhances hydrolysis and olation. If sufficient alkali is present for 100 per cent diol complexes, sulfate ions reduce further olation by repressing hydrolysis. The apparent contradiction is explained by assuming a high degree of stability for ring complexes involving either a diol bridge between two chromium atoms or a bridge composed of one olated OH group and one coordinated sulfate group between two chromiums. The coordination of sulfate ions to chromium follows a stepwise pattern of stability constants which can be explained on structural grounds. High stability constants of the order of at least 2000 appear to be associated with six membered rings involving one olated OH group and one coordinated sulfate group. Coordination of an additional sulfate group to this ring, to form a double ring, appears to have a stability constant of the order of 10 to 140, while other types of sulfate coordination such as monodendate attachment or four membered ring formation appear to be very unstable. Whole numbered ratios between chromium and coordinated sulfate groups published by past workers are fortuitous results of the choice of suitable concentrations assisted by wide gaps in stability constants due to types of complex which can be formed. In the absence of other coordinating ligands than water and hydroxy groups, the freshly boiled chromium complexes are highly colored and change to less colored complexes on boiling with sulfate. In the case of the two thirds basic complex, this is completely soluble; but a precipitate forms on boiling with sulfate

ions. These changes are attributed to changes from a small diol complex with a stable highly resonating ring structure, to an enlarged complex required for stable coordination of sulfate groups. The mechanism suggested is the progressive displacement by sulfate of a small proportion of olated hydroxy groups, which olate with neighboring molecules to form enlarged molecules, these being lower in solubility and average color per chromium atom. There is evidence to suggest that a sulfate ion does not form a stable six membered ring with two chromium atoms already bridged with two hydroxy groups. Models show that such a double ring involves a greater distortion of normal bond angles than a double ring involving two sulfate groups and one hydroxy group linking two chromium atoms. Conductrimetric evidence that alkali displaces coordinated sulfate immediately from the chromium complex has been confirmed by another investigator. This may be due to rapid diol formation or merely to an inherently lower sulfate affinity for a more basic chromium atom. R. H. T.

Leather and Tanning Materials. X. Estimation of Tannin by Adsorption on Polyamides. By Hans Batzer. *Das Leder* **5,** 25 (1954). A material for tannin analysis that would adsorb tannin from a mixture of related compounds would be desirable, especially one that would form a definite compound with tannin. Polyamides appear promising. Such an adsorbent, however, must be tested against all tanning materials by several analysts; this has not yet been done. Ultramid 6A (BASF) is made from 60 per cent adipic acid-hexamethylene diamine salt, 40 per cnet caprolactam and a small amount of adipic acid as a chain breaker. Ultramid 6A gave the same type of adsorption curve as hide powder when milligrams of adsorbed tannin was plotted against milligrams of nitrogen in the adsorbent. Granular Ultramid 6A did not adsorb tannin, but an adsorbent, fibrous form was prepared by dissolving the material in hot methanol and precipitating it in water with violent agitation (see also Gustavson *This Jour.* **47,** 700 (1952). Tannin analyses are made by two methods: the shake and the filter method. A comparison of these two methods, with hide powder, gave the following values for ratio of tannin by the shake method to that by the filter method; Tannin DAB VI, 0.92; quebracho, 0.91; oak wood, 0.89; spruce bark, 0.82; lignin tannin, 0.68. Analyses by both methods with Ultramid 6A and hide powder gave the following tannin values:

	Filter method		Shake method	
	Hide powder	Ultramid	Hide powder	Ultramid
	%	%	%	%
Quebracho	45.8	44.4	41.9	42.4
Chestnut wood	73.7	72.8	—	—
Valonia	68.4	65.0	—	—
Oak wood	69.7	66.7	62.4	63.0
Wattle bark	71.3	71.6	—	—
Sumac	31.1	29.2	—	—
Spruce bark	25.1	21.1	—	—
Lignosulfonic acid tan	64.6	30.3	61.2	24.5
Auxiliary syntan	53.4	19.4	39.4	15.6

The solubility of hide powder is a disadvantage that is almost absent with Ultramid. A lignosulfonic acid tan containing 2.70 per cent nitrogen, was analyzed by both methods. The hide powder nontannin, by the filter method, contained 11.0 per cent nitrogen, and the Ultramid nontannin, 3.25 per cent. The corresponding values by the shake method were 8.1 and 3.3 per cent respectively. I. D. C.

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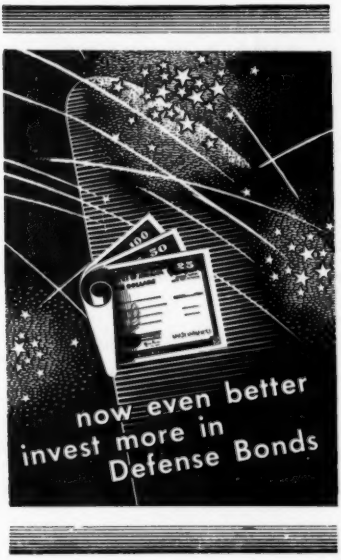

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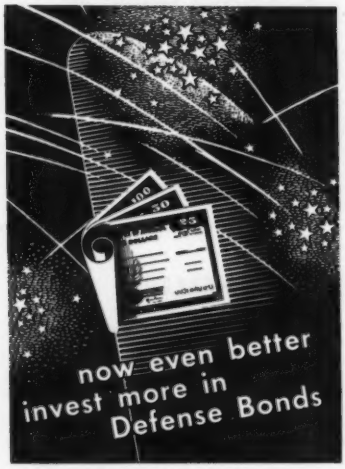

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